

*April, 1930*

# RUBBER CHEMISTRY AND TECHNOLOGY

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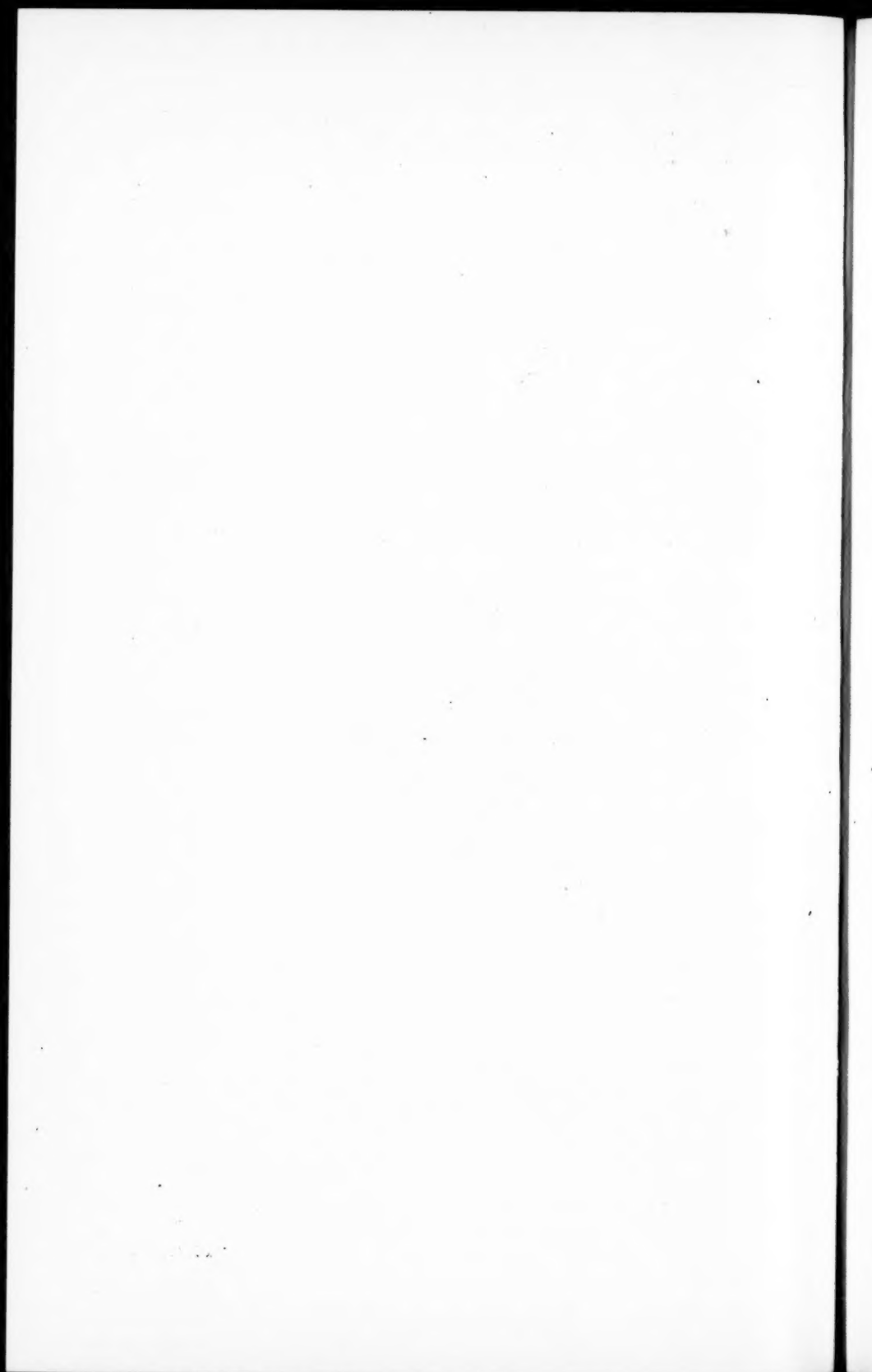
*Published under the Auspices of the*  
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY

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VOLUME III

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# RUBBER CHEMISTRY AND TECHNOLOGY

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of the American Chemical Society,  
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Editor.....C. C. DAVIS  
Associate Editor.....H. L. FISHER  
Secretary-Treasurer.....H. E. SIMMONS

Vol. III

April, 1930

No. 2

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions; back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

# Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

## The Rubber Division of the American Chemical Society

### Officers

Chairman.....STANLEY KRALL, Fisk Rubber Co.  
Vice-Chairman.....H. A. WINKELMANN, Philadelphia Rubber Works Co.  
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio  
Executive Committee..N. A. SHEPARD, W. A. GIBBONS, L. B. SEBRELL, IRA WILLIAMS, HAROLD GRAY  
Sergeant-at-Arms.....E. R. BRIDGWATER

## Local Group Activities

### Akron Group

*December 9, 1929.* Address by W. K. Lewis (Mass. Institute of Technology) on "The Amorphous State."

*Feb. 17, 1930.* Address by H. C. Young (Chas. MacIntosh & Co., Manchester, England) on "Some Engineering Problems of Rubber."

Discussion by R. R. Jones and H. K. Jennings (Firestone Tire & Rubber Co.), "Horse Power vs. Man Power." E. E. Davison (B. F. Goodrich Co.), "Tubing Machines." Roy W. Brown (Firestone Tire & Rubber Co.), "Mill Cooling." A. P. Regal (Philadelphia Rubber Works), "Anti-Friction Bearings." J. Grotzinger (Goodyear Tire & Rubber Co.). W. H. Welch (Goodyear Tire & Rubber Co.). W. E. Waters (Goodyear Tire & Rubber Co.), "Multiple vs. Single Story Factories." H. H. Baird (Goodyear Tire & Rubber Co.), "Ventilation."

New Officers of the Akron Group are as follows: *Chairman*, C. W. Sanderson (Goodyear Tire & Rubber Co.); *Vice-Chairman*, W. E. Shively (Goodyear Tire & Rubber Co.); *Secretary-Treasurer*, L. W. Brock (Godfrey L. Cabot Co.).

### Chicago Group

*Jan. 17, 1930.* Addresses by L. J. D. Healy (Fisk Rubber Co., Cudahy, Wis.) on "Modern Developments in Control Instruments for Rubber Factories." R. E. Olson (Taylor Instrument Cos., Rochester, N. Y.) on "Recently Developed Instruments for Tire-Vulcanizing Processes." E. L. Stilson (Bristol Co., Waterbury, Conn.) on "Modern Developments in Instruments for the Rubber Industry."

### New York Group

*Dec. 16, 1929.* Addresses by R. P. Dinsmore (Goodyear Tire & Rubber Co.) on "Rubberizing Balloon Fabrics." A. R. Davis (Firestone Footwear Co., Hudson, Mass.) on "Rubber-Fabric Combinations as Used in Rubber Footwear." K. E. Burgess (Richards & Co., Stamford, Conn.) on "Rubber-Pyroxilin-Textile Combinations." W. L. Sturtevant and D. P. Weisberg (Raybestos-Manhattan, Inc.) on "Technology of Rubber-Textile Combinations with Reference to Transmission Belting." T. M. Knowland (Boston Woven Hose & Rubber Co.) on "The Strength and Stretch of Double Texture Rubber Goods." R. R. Lewis (C. Kenyon Co., Brooklyn, N. Y.) on "The Effect of Proofing Processes on the Tensile Strength of Fabrics."

The new officers are: *Chairman*, W. L. Sturtevant (Raybestos-Manhattan, Inc.); *Vice-Chairman*, Kenneth Soule (Raybestos-Manhattan, Inc.).

#### Los Angeles Group

*December 20, 1929.* Address by E. W. Matthis (Pacific Goodrich Rubber Co.) on "The Goodrich System of Wage Payment."

New officers are: *President*, F. W. Stavely; *Vice-President*, F. S. Pratt; *Secretary-Treasurer*, W. R. Hucks.

*February 26, 1930.* Addresses by Harrison E. Howe on "Alcohols New and Old," and by F. W. Stavely on "The Rubber Industry of Los Angeles."

### Report of the Treasurer of the Rubber Division

Money in the bank December 1, 1929.....	\$ 304.17	
Money received from the New York Group.....	250.00	
Money received from dues.....	1577.44	\$2131.61
<hr/>		
Expenditures:		
Postage and telegrams.....	\$ 12.27	
Translations.....	125.85	
Mack Printing Co.....	2.58	
Ben Franklin Printing Co.....	68.50	
October issue—India Rubber World.....	207.25	
Palmerton Publishing Co.....	94.32	
Refunds.....	36.00	
Mimeographing abstracts of spring meeting in Atlanta.....	9.00	
Stenographic services.....	30.00	585.77
<hr/>		<hr/>
On hand March 19, 1930.....		\$1545.84

H. E. SIMMONS, *Secretary-Treasurer*

#### Corrections

An article entitled "On the Permeability of Rubber Mixings," by W. CECIL DAVEY and T. OHYA on pages 96-98 of RUBBER CHEMISTRY AND TECHNOLOGY, January, 1930, failed to acknowledge the source of the article. This article was reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 5, No. 1, pages 27-30, June, 1929.

The article by Scott which begins on page 3 of the January, 1930 issue of RUBBER CHEMISTRY AND TECHNOLOGY was reprinted from the *Transactions of the Institution of the Rubber Industry*.

## New Books and Other Publications

**The Colloid Chemistry of Rubber.** Paul Stamberger. Published by the Oxford University Press, London and 114 Fifth Ave., New York City, 1929. 88 pages. \$2.00.

The second and, it is to be regretted, presumably the last series of Gow lectures on "The Colloid Chemistry of the Rubber Industry" were delivered in November, 1928, and the present volume is the published account. That the subject-matter is comprehensive is shown by the chapter titles:

- I. Colloid Chemistry and Colloids.
- II. Colloid Properties of Rubber, Rubber Latex and Its Industrial Applications.
- III. Lyophile Colloids (Gels). Crude Rubber and Its Solvation.
- IV. Compounding. Compounding Ingredients. Rubber Substitutes. Synthesis of Rubber.
- V. Vulcanization. Devulcanization. Recent Views on the Structure of Rubber.

The author has just failed to produce an interesting book, for it makes somewhat difficult reading even to one familiar with rubber chemistry. Where, however, the author treats of his own work, particularly in Chapters III and IV, dealing with organophilic sols of rubber and the behavior of fillers the statements are more connected and make easier and more interesting reading.

The book should be of value chiefly to those colloid chemists who desire to study the chemistry of rubber. The book is well printed and bound. [H. P. STEVENS in the Bulletin of The Rubber Growers' Association, February, 1930.]

**Rubber Research in Holland.** By Dr. A. Van Rossem. Published by the Netherlands Government Rubber Institute, Poortlandlaan 35, Delft, Holland. 1929. 12 pp. For free distribution.

Established in 1909, the Netherlands Government Rubber Institute has for twenty years been carrying out special investigations, testing work and research studies for the benefit of the rubber industry. Its studies of the freezing of raw rubber, the composition of the acetone extract of raw rubber, the calender effect of masticated rubber, and of the first period of the oxidation process of vulcanized rubber are well known. This review of the history and scope of the institute is reprinted from the recent International Issue of the *India-Rubber Journal*. [From *The Rubber Age* of New York.]

**"Gummi-Kalender 1930."** Jahrbuch der Kautschuk-Industrie. Ein Hilfsbuch für Kaufleute, Techniker, Händler und Reisende der Kautschuk, Asbest- und Celluloid-Branche. Edited by Ernst A. Hauser and Kurt Maier. Published by Union Deutsche Verlagsgesellschaft, Zweigniederlassung, Berlin. Cloth, 37/8 by 57/8 inches, 454 pages.

The "Gummi-Kalender 1930" is the fifteenth edition of this year book for merchants, technicians, dealers, and salesmen of the rubber, asbestos, and celluloid industries. As usual, the information in it has undergone careful revision. Thus the technical section in Part I contains directions for the newest methods of physical testing in connection with rubber mixings. Then there is a short review of the progress of rubber research during 1928-29.

Many of the calculation tables have been amplified and, where necessary, completely rearranged. The chapter on the most important compounding ingredients

for rubber has been thoroughly revised, and the statistical data have been brought up to date and new tables have been included. Thus we find an interesting table concerning production in the German tire industry during 1928. Once more the editors have succeeded in compiling a useful and handy little reference book. [From *India Rubber World*.]

**"Native Rubber in the Dutch East Indies, Report to The Rubber Growers' Association."** By V. A. Tayler and John Stephens. Issued by The Rubber Growers' Association, Inc., 2-4 Idol Lane, Eastcheap, London, E. C. 3, England. Paper, 48 pages, 6 by 9<sup>3</sup>/<sub>4</sub> inches. Map and numerous illustrations.

This report embodies the results of a systematic survey by organized plantation interests of rubber production by native growers. The work was undertaken to obtain first-hand information on the extent, condition, and possible future output of native-grown rubber.

The investigators' field work covered conditions in the Residencies of Pontianak and Banjarmasin in Borneo and of Lampongs, Palembang, and Jambi in Sumatra. Their findings in each Residency are reported under geography and topography, population, climate, communications, cultivation, rubber, planted area, tapping output, preparation and marketing, labor and future production, and economic position.

The results of their study are presented in a summary of estimates tabulating planted areas and potential as distinguished from probable outputs for the years 1929 to 1933 inclusive. [From *India Rubber World*.]

**"Guide to the Preparation of Plantation Rubber in Ceylon."** This indexed book of 60 pages by T. E. H. O'Brien is issued by the Rubber Research Scheme (Ceylon). The work discusses approved field and factory operations for the conduct of tapping and collecting latex and the preparation of the various standard grades of plantation rubber. [From *India Rubber World*.]

**"U. S. Heavy Service Tire Manual and Changeover Guide."** This well-indexed handbook, now in its second edition, was prepared and issued by the Technical Service Division, United States Rubber Co., Detroit, Mich. The book is replete with original data on selection, sale, servicing, and proper tire equipment for heavy motor transportation service.

It contains a special section devoted to the subject of changing over vehicles from solids to pneumatics and from high-pressure tires to balloons. In it are discussed changeover considerations and methods, supplemented by data for vehicle analysis and proper tire sizes. [From *India Rubber World*.]

**Cotton Facts—1929.** Published by Shepperson Publishing Company, 44 Whitehall Street, New York City. 1929. 256 pp.

The extent of the use of cotton and cotton products in the rubber industry makes accurate data on that commodity almost as necessary as statistics on rubber itself. Information for the United States and other countries as well is included in this 54th edition of a standard compilation of essential figures on crops, receipts, stocks, exports, imports, visible supply, sales, prices, consumption, and manufacturing output. [From *The Rubber Age* of New York.]

**Synchronous Motors.** Published by the General Electric Company, Schenectady, N. Y. November, 1929. 90 pp. For free distribution.

A general trend toward the use of synchronous motors for rubber factory machine drives to operate at line-shaft speeds came early in the last decade along with the impetus given to the use of synchronous motors in industry at large. Descriptions and illustrations of installations in rubber factories are to be found



in this volume, together with a general outline of the use of such motors. [From *The Rubber Age of New York.*]

**Annual Report of Director of the Bureau of Standards.** By George K. Burgess. Published by the Government Printing Office, Washington, D. C. 1929. 60 pp. \$0.10.

Details of the more important research work done by the Bureau of Standards during the year are given in this report. Industrial research accomplished by the bureau included abrasions tests for rubber, a survey of the manufacture of sponge rubber, a report on the properties of rubber floor tile, and a study of rubber insulating materials. The Rubber Division of the American Chemical Society coöperated with the bureau and has furnished a research associate to work at the bureau. [From *The Rubber Age of New York.*]

**"Twenty-ninth Year Book—1929,"** issued by The Rubber Manufacturers Association, Inc., lists the names of its officers, board of directors, standing committees, and firm members of the various divisions of the Association. Three supplemental pages record the Association necrology for 1929. [From *India Rubber World.*]

**"The Rubber Exchange of New York, Inc., Fourth Annual Report, 1929."** This report is submitted by F. R. Henderson, president of the Rubber Exchange, who summarizes the activities of the year's dealings from September 1, 1928 to August 31, 1929. The total number of contracts on the exchange for the year was 188,132 or 470,330 tons, representing a value of \$217,000,000. Transferable notices, representing deliveries of physical rubber, amounted to 7937 lots, equivalent to 19,842½ tons, an increase of 24 per cent. over last year's deliveries. [From *India Rubber World.*]

**"Rubber Producing Companies—1929."** Compiled by The Mincing Lane Tea and Rubber Share Brokers Association, Ltd., 1929, London. Published by *The Financial Times, Ltd.*, 72 Coleman St., London, E. C. 2, England.

This annual is a complete and authoritative collection of data for the information of the investor in British controlled rubber and tea estates. The material given includes lists of officials, capital, acreage, tenure, purchase price, accounts, production, forward sales, dividends, highest and lowest prices of shares, etc. [From *India Rubber World.*]

**"Dealers' Stocks of Tennis Shoes in the United States."** Special Circular No. 2534, Rubber Division Dept. of Commerce, Washington, D. C. The object of this survey is to determine the carryover of stocks by dealers at the end of the season. [From *India Rubber World.*]

**"Foreign Markets for Rubber Boots, Shoes, Heels, and Soles."** Section IV, European countries. Rubber Division, Dept. of Commerce, Washington, D. C. [From *India Rubber World.*]

**Rubber Facts and Figures.** Published by F. C. Mathieson & Sons, 16 Copthall Avenue, London, England. 1929. 2s.

The prices of shares of rubber plantation companies and concise data on the properties, crops, capital, dividends, etc., of these companies are summarized in this 41st edition of what is now regarded as a standard publication on the subject. [From *The Rubber Age of New York.*]

**"The Next Five Years in American Business Profits. II—The Automobile Tire Industry."** This 18-page pamphlet is a special supplement of "Trade and Securities Service" issued by Standard Statistics Co., 200 Varick St., New York, N. Y. It presents a masterly discussion and analysis of the tire industry, its trend, gravest problems, and their solutions, supplemented by a chapter on profits and

security values. This comprehensive statistical study will prove enlightening to tire manufacturers, dealers, motorists, and the investing public. [From *India Rubber World*.]

**"The British Rubber Industry."** Special Supplement, November 19, 1929. *The Daily Telegraph*, London. In this 40-page issue the technical and trade aspects as well as general forms of rubber manufacture other than tires are comprehensively treated by well-known rubber chemists and manufacturing authorities. Articles of chief interest include: rubber supply, modern plantations, new services for rubber, vulcanization and research, mixing practice, flooring and tiling, rubber in the household, in garments, footwear, and sports, salesmanship and marketing, and London as a rubber market. [From *India Rubber World*.]

**"Die Lage der Kautschukmarktes in der Nachkriegszeit."** By Dr. Heinz George. Published by Wilhelm Christians Verlag, Berlin S. W. 19. 1929. Stiff paper, 6 by 8 inches, 150 pages. Tables. Bibliography.

In the present book, Dr. George discusses the problems that have confronted the rubber industry since the end of the war. Starting from the beginning of the industry, he introduces the reader, in a preliminary chapter, to the various rubber bearing plants and the development of rubber cultivation up to the end of the war, indicating the various uses of rubber. Then follows the book proper divided into two parts, a conclusion, and an appendix. Part I describes the slump, its causes, and the various attempts to remedy it until the Stevenson Scheme was introduced.

In Part II the working of this scheme is handled—its effects on production, price, consumption; the American consumers and their counter measures; defects of the scheme. The final portion is devoted to a survey of the market condition since the abolition of restriction and a discussion of the future in which the conclusion is reached that possibly the solution of the rubber problem may yet be found in synthetic rubber. Several tables are appended including one in which the financial position of sixty rubber producing companies is analyzed. A list of the various publications consulted is also added. [From *India Rubber World*.]

**A Picture of World Economic Conditions in the Summer of 1929.** Published by the National Industrial Conference Board, Inc., 247 Park Avenue, New York City. 1929. 320 pp. \$2.50.

An analysis of the condition of industry and trade in twenty-two foreign countries and the United States, this work is divided into two parts. The first section presents and interprets the major statistics of industrial production, wages, and employments, prices, etc., while the second part is a compilation of nineteen special articles from an eminent group of foreign correspondents, all of whom are authorities on the economic life of their respective countries. Alberto Pirelli, head of the rubber company which bears his name, is, for example, a correspondent in Italy. Of especial interest is an article on "The Relation of Colonies to Dutch Economic Life" by E. Heldring, president of the Royal Netherlands Steamship Company, which describes the importance of rubber production in the Netherlands East Indies and balata production in the Netherlands West Indies. [From *The Rubber Age of New York*.]

**"National Waste Review."** Published by the Trade Promotion Bureau of the National Association of Waste Material Dealers, Inc., 1109 Times Building, New York, N. Y. Paper, 68 pages, 8½ by 11½ inches.

The first issue of this monthly magazine is dated January, 1930. Its publication is authorized by the Board of Directors with the thought that it will serve as a means of presenting the Association and its aims to dealers, consumers, and producers of waste material throughout the world. The contents comprise regular



features devoted to waste trade problems, market reviews, new firms and corporations, and traffic information, followed by a Salvage and Reclamation Section, which includes clearing house offerings of machinery.

The scope of service proposed for this magazine is broad and extremely important industrially. It has received the endorsement of the leaders in the waste trade. [From *India Rubber World*.]

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# A Survey of Recent Literature on the Chemistry of Rubber

## Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the January 10 and 20, February 10 and 20, and March 10 and 20, 1930, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Do not forget Lüdersdorf. LEO ECK. *Gummi-Ztg.* 43, 2868-9(1929).—Historical. Attention is called to certain attempts, notably those of Lüdersdorf and of van Geuns, antedating those of Goodyear and Hancock, to change the properties of rubber by means of S. C. C. DAVIS

The combination of sulfur and rubber. FELIX FRITZ. *Gummi-Ztg.* 44, 23(1929). Historical. Comments on the same subject as that of Eck (see preceding abstr.). C. C. DAVIS

Rubber compounding practice. WEBSTER NORRIS. *India Rubber World* 81, No. 2, 54-7(1929); cf. *C. A.* 23, 5610.—Ingredients for special uses, including surface finishes, dry lubricants, abrasives, fibrous tougheners and substances resistant to acids, oil and heat are discussed. C. C. DAVIS

Tables for the proportions of sulfur and accelerator to be added to rubber mixtures. WERNER ESCH. *Gummi-Ztg.* 44, 80, 82(1929).—From a practical point of view and subject to various restrictions, the more accelerator used in a rubber mixt. the less the S required, and *vice versa*. It may therefore be of convenience to utilize tables which show the proportion of accelerator for various proportions of S over a range of S from very low to very high for the particular accelerator. In the present paper such tables for tetramethylthiuramdisulfide, tetramethylthiurammonosulfide, "Vulcanol," "Doptax," mercaptobenzothiazole, "Safex," diphenylguanidine, ethylidene-aniline and hexamethylenetetramine are given. C. C. DAVIS

Study of the heat exchange in bodies and the application to rubber. G. BRUHAT. *Rev. gén. caoutchouc* 6, No. 55, 3-13(1929).—Largely mathematical; the subjects include the phys. laws of heat transmission, general equations of cond. and the heating and cooling of com. rubber products. C. C. DAVIS

The coefficients of friction between rubber and other materials. Frictional grip of rubber-tired wheels. R. ARIANO. *India Rubber J.* 78, 351-3(1929).—A translation of *Il politecnico* No. 5, 1929. C. C. DAVIS

An enquiry into the use of reclaimed rubber. F. JACOBS. *Déchets et régénérés* 1, No. 3, 2(1929); cf. Panem, *C. A.* 23, 5611.—Reclaimed rubbers must not be considered as substances similar to new rubber. PAUL BARY. *Ibid* 2-3.—It seems desirable to dispense with the use of softeners in reclaiming rubber, so that their softening action will not mask the attainment of a true plasticizing of the scrap. C. C. DAVIS

The rational use of scrap and reclaimed rubber. The manufacture of industrial rubber products. H. BAUFARON. *Déchets et régénérés* 1, No. 3, 4-5(1929); cf. *C. A.* 23, 4373.—Typical formulas for various kinds of molded products are given. C. C. D.

Rubber in the printing industry. JOHN HELFRICH. *India Rubber World* 81, No. 2, 61(1929).—The uses of rubber for inking rollers, offset blankets, printing plates and various accessories are described and illustrated. C. C. DAVIS

Progress in the use of rubber linings for acid leaching tanks. HARLAN A. DEPEW. *India Rubber World* 81, No. 2, 69(1929).—The expts. are a sequence to previous work already described (cf. D. and Lewis, *C. A.* 21, 512). Failure of linings was most pronounced near the surface of the liquid where atm. O could attack them and where at the same time a high temp. prevailed. An improved method of lining tanks is described, which has the novelty of painting a soln. of highly active accelerator on alternate rubber layers. The accelerator then migrates sufficiently so that a homogeneous product is obtained. C. C. DAVIS

**Uses of rubber in modern aircraft. I. Rubber in airplane construction.** JOHN F. HARDECKER. *Rubber Age* (N. Y.) 25, 485-7(1929).—An illustrated description. **II. Rubber in airplane landing gears.** *Ibid* 607-10.—Illustrated. **III. Rubber in aircraft power plant and radio installations.** *Ibid* 667-9.—Illustrated. C. C. DAVIS

**Manufacture of ebonite plates for the radio industry.** FRANCK A. BATH AND ANDRÉ FRASER. *Rev. gén. caoutchouc* 6, No. 55, 15-20(1929).—An illustrated description. C. C. DAVIS

**A simple test of the electric insulating power of rubber.** MAX SPETER. *Gummi-Ztg.* 43, 2918(1929).—The test which is described and illustrated is based on the ability of the rubber to discharge an electroscope. C. C. DAVIS

**The coagulation of latex.** (MRS.) N. BEUMÉE-NIEUWLAND. *Arch. Rubbercultuur* 13, 555-65(1929). (In brief form in English 566-7).—In connection with the idea of de Vries that latex is a negatively charged colloid with a low degree of solvation (cf. *C. A.* 19, 419) it is pointed out that latex shows some phenomena characteristic of lyophilic colloids but others characteristic of lyophobic colloids. In such systems the properties of 1 type are dominant and this is the protective colloid. Latex is then a system of lyophilic protein colloids protecting the lyophilic rubber globules. The 2nd liquid zone of Whitby, de Vries and Belgrave is explained by a change from mol. proteins to acid proteins. Latex freed of protein (by creaming, centrifuging or alkali) should then show no "irregular series," which was found to be the case. When the protein is removed from latex mechanically (creaming or centrifuging) or chemically (NaOH), coagulation by acids is very rapid, and the rubber dries slowly and shows a low tensile strength. Rubber from "underlatex" (after centrifuging), with a high % N, shows normal or high tensile strength. Latex freed of protein by alkali or by creaming does not flocculate after 1:9 diln. and heating (B mixt.). After addn. of acid a coagulum is formed. Addn. of protein, e. g., casein, to protein-free latex gives rubber with abnormally high stiffness, while the tendency to become tacky disappears and the rate of drying increases. The  $p_H$  of latex coagulation is the same as the  $p_H$  of protein pptn. (albumin 4.7, globulin 5.4), indicating a certain role played by the proteins in coagulation. After calling attention to the lipid theory of Overton and the investigations of Höber (*Physik. Chemie der Zelle und Gewebe* 1924; cf. *C. A.* 19, 996) recent literature on lipoids and sterols is reviewed, and the possibility considered that in latex a layer of lipoids covers the rubber globules and plays an important role. Preliminary expts. show that cholesterol coalesces B mixt. A hypothesis suggests that latex proteins are protective colloids, while lipoids (sterols, lecithin to protect the sterol, sterol esters) are present as a layer around the probably viscous interior of the globules, i. e., globules suspended in a protein emulsion with a lipid covering layer and a viscous interior. In ordinary coagulation at  $p_H$  4.8 the proteins would then flocculate and form a gel in which the globules would remain suspended. The limit of flocculation of lipoids is probably lowered by proteins (as is shown for lecithin), and as soon as protein and lecithin, both hydrophilic, are flocculated, only the hydrophobic sterol remains. This is then readily flocculated by salts present, so that the globules themselves are no longer protected but remain enclosed in the gels. The latter flocculation is irreversible, and is the reason that coagulation cannot be undone. C. C. DAVIS

**Quebrachitol from the serum of Hevea latex.** T. G. LEVI. *Gazz. chim. ital.* 59, 550-2(1929).—The method developed by Contardi (cf. *C. A.* 19, 1135) for isolating quebrachitol from latex serum can be simplified and made more economical in the following way. Ppt. the proteins in the serum by adding tannic acid (5 g. of tannin per kg. of serum), eliminate all water by evapn., dissolve the residue in glacial AcOH (equal wt.), and allow the soln. to stand until no more quebrachitol crystallizes out (12.5 g. per kg. of serum). It is practically pure. With slab rubber the proteins have been destroyed during maturation, so with this serum tannin need not be added. However, during the evapn. of slab rubber serum,  $MgNH_4PO_4$  is deposited and must be filtered before completing the evapn. The procedure is then the same as before, the yield from the 1st deposition of pure quebrachitol being 12 g. per kg. of serum. Inositol hexaisovalerate and inositol hexapalmitate were prepd. by the method of Moldavskii (cf. *C. A.* 20, 2831) and were found to m.  $151^\circ$  and  $83^\circ$ , resp., instead of  $137^\circ$  and  $75^\circ$  found by M. Besides these, 3 new esters were prepd. *Quebrachitol pentaisovalerate*,  $(C_{15}H_{31}CO_2)_5C_6H_6O$ , prepd. by refluxing quebrachitol (1.95 g.) with isovaleryl chloride (6.10 g.), is liquid at ordinary temp. *Quebrachitol pentalaurate*,  $(C_{11}H_{23}CO_2)_5C_6H_6O$ , prepd. by heating quebrachitol (1.95 g.) with lauryl chloride (11 g.) at  $120-60^\circ$  in *vacuo* and crystg. from EtOH, m.  $32^\circ$ . *Quebrachitol pentapalmitate*,  $(C_{15}H_{31}CO_2)_5C_6H_6O$ , prepd. by heating quebrachitol (1.95 g.) with palmityl chloride (14 g.) at  $120-60^\circ$  in *vacuo* and crystg. from EtOH, m.  $58^\circ$ . C. C. DAVIS

**Quality, control of raw materials and stocks in process.** WALTER J. GELDARD.

*Rubber Age* (N. Y.) 26, 192-3, 203(1929).—An illustrated description of sampling, specifications, etc. C. C. DAVIS

Steam production and economy in the rubber factory. G. B. WILLIAMSON. *Trans. Inst. Rubber Industry* 5, 119-38(1929). C. C. DAVIS

Toxic substances in the rubber industry. P. A. DAVIS. *Rubber Age* (N. Y.) 25, 199-200(1929); cf. C. A. 23, 5610.—This instalment deals with hexamethylenetetramine. C. C. DAVIS

Comparison of acetylene black with gas black and lampblack. WERNER ESCH. *Gummi-Ztg.* 44, 301(1929).—Comments on an article by Dawson (cf. C. A. 23, 5351). C. C. DAVIS

Some new carbon blacks. W. B. WIEGAND. *Can. Chem. Met.* 13, 269-70 (1929).—A brief description of some new varieties of carbons involving elimination of the selective adsorption of C black for org. accelerators. Grade 1 AA represents an intermediate stage of inactivity and 1 AAA represents an advanced stage where adsorptive activity for rubber accelerators is practically eliminated. Tables illustrate possible accelerator economies by the use of these carbons, whose textures and milling properties appear broadly indistinguishable from those of standard C blacks. The new black shows, concomitantly with reduced adsorption of accelerator, lower moisture, lower volatile matter, lower KOH adsorption, higher content of pure C, lower H and lower O content. These blacks are definitely purer than the old, with a reduced, instead of increased, adsorptive activity. Adsorptive activity, whether toward accelerators, moisture, gases or alk. solns., can be controlled at will over a range of temp. (600-1100°) by the extent to which O is excluded during the heating process. A theory relative to the activity of ordinary carbon black is advanced, and a brief bibliography appended. W. H. B.

Hardness test for rubber with the apparatus of the Gesellschaft für Feinmechanik m. b. H. ANON. *Rev. gén. caoutchouc* 6, No. 55, 24-5 (1929).—A new instrument is described and illustrated. C. C. DAVIS

Uses of rubber in modern air craft. IV. Rubber in lighter-than-air craft and for safety and comfort in modern aviation. JOHN F. HARDECKER. *Rubber Age* (N. Y.) 26, 29-31 (1929); cf. C. A. 24, 263.—An illustrated description. C. C. DAVIS

Contributions from the Rubber Research Scheme, Ceylon. Imperial Institute. ANON. *Trop. Agr.* (Ceylon) 72, 206-16(1929).—Rubber trees must be sprayed with Bordeaux mixt. with the greatest care as a trace of Cu in the latex deteriorates the rubber made from it. Plasticity and artificial aging tests on rubber prepd. from latex gathered while the trees were being sprayed with Bordeaux indicate that no harm will result if care is exercised and the weather is clear. The extrusion and compression tests for plasticity were critically examd. The rate of extrusion not only varies with the plasticity but also with the load and the diam. of the orifice. Crepe from very dil. latex was shown by expt. to be softer and to require slightly less mastication than that from undil. latex. Samples of rubber more than 2 years old, which contained low proportions of fatty acids, showed great variability when vulcanized. None of 39 samples less than 2 yrs. old showed any variation of importance when the mixt. consisted of rubber 90, S 5, ZnO 5 and accelerator 1. When fatty acids were absent from the rubber, unsatisfactory results were obtained. Both hexamethylenetetramine and diphenylguanidine were used as accelerators with like results. The conclusions drawn by the Imperial Inst. as a result of their work on accelerator mixings are at variance with those of Dinsmore and Zimmerman (C. A. 20, 1004). It is thought this is due to the latter using much lower proportions of S and accelerator. The crit. ratio between accelerator and S varies with the rubber and this may be due to the serum substances. Variability can be entirely eliminated in first-grade rubber by the right proportion of S and accelerator. A. L. M.

An enquiry into the use of reclaimed rubber. H. BAUFARON. *Déchets et régénérés* 1, No. 4, 8(1929); cf. C. A. 23, 5611.—Reasons are given to show why reclaimed rubbers are of advantage even when the price of new rubber is very low. C. C. DAVIS

Reclaimed rubber, old rubber and latex. E. A. HAUSER. *Déchets et régénérés* 1, No. 4, 2-3(1929).—Water dispersions of scrap and of reclaimed rubber offer new possibilities in the use of latex, for by combining the 2 liquids, dispersions of various properties and of low cost impossible to obtain with latex alone can be prepd. This subject is discussed in its various present and future aspects. C. C. DAVIS

The rational use of scrap and reclaimed rubber. The manufacture of industrial rubber. H. BAUFARON. *Déchets et régénérés* 1, No. 4, 6-7(1929); cf. C. A. 24, 263.—Numerous formulas of rubber mixings contg. scrap or reclaimed rubber suitable for use in tube machines are given. C. C. DAVIS

Substance resembling gutta-percha and coming from the Tu-chung tree. S. MINATOYA AND K. ISHIGURO. *Caoutchouc & gutta-percha* 26, 14765(1929).—See C. A. 23, 5060. C. C. DAVIS

Gutta-percha and balata resins and their uses. F. HARRIS COTTON. *India*

*Rubber J.* 78, 531-2, 534 (1929).—A general description covering the sources and qualities of com. grades, their chem. properties, uses for rubber softeners, golf ball cores, rubber reclaiming, belt dressings, fly-paper, tree banding mixts., chicle substitutes and pyroxylin lacquers, and hardening processes. The use of these resins in the cellulose lacquer and enamel industry is very promising. Expts. show that the resins dissolve readily (without sepn. of waxes) in the ordinary mixed solvents, giving non-blushing lacquers. The use of the soft resins dispenses with the usual plasticizers. Coumarone resin gives lacquers which tend to blush, but its partial replacement by gutta-percha resin eliminates this tendency. In general these resins seem preferable to damar and ester gums. A good lacquer contains: dry pyroxylin (0.5 sec.) 6, dry pyroxylin (5-10 sec.) 6, hard gutta-percha resin 12, EtOAc, 37.5, BuOAc 12.5, EtCO<sub>2</sub>Bu 18.75, BuOH 25, C<sub>6</sub>H<sub>6</sub> 75, PhMe 50.

C. C. DAVIS

**Some notes on artificial aging tests for rubber.** W. W. VOGR. *Ind. Eng. Chem.* 21, 1015-6 (1929).—No present artificial aging test duplicates natural aging closely enough to allow the use of correlation factors, for the latter depend upon the particular property, the changes in which are measured comparatively. It is, however, possible to obtain useful information on the natural aging of a rubber mixt. in darkness by detg. independently its resistance to oxidation by a high-pressure O test and its other internal changes (after-vulcanization, etc.) by heating it in N. For rubber products which age under other conditions, still further independent tests must be made to accentuate each influence and suppress the others. For studying the aging of mixts. where oxidation is the predominant factor, increases in wt. in the artificial test give better results than other methods.

C. C. DAVIS

**Correlation between Geer oven and natural aging of selected tire compounds.** A. H. NELLEN AND H. M. SELLERS. *Ind. Eng. Chem.* 21, 1019-20 (1929).—In aging tests of tire tread and carcass mixts., 4 and 8 days in the 70° Geer oven corresponded to approx. 1 and 2 yrs., resp., of natural aging. On the other hand 12 days in the oven did not correspond to 3 yrs. of natural aging. The tensile product showed the best correlation between the oven test and natural aging.

C. C. DAVIS

**The swelling of vulcanized rubber in liquids.** J. R. SCORR. *Trans. Inst. Rubber Industry* 5, 95-118 (1929).—Swelling was measured by immersing the sample in the liquid at const. temp. (25°) in darkness. By assuming the increase in wt. to be the liquid absorbed, and knowing the d. of liquid and of rubber sample, the swelling was the vol. of liquid absorbed in percentage of the vol. of the original sample. The mechanism of absorption is not discussed. Expts. with 15 liquids showed that the vol. of swollen rubber was practically the same as the sum of the vols. of original rubber and liquid absorbed after allowing for extd. substances. Time-swelling curves show that an initial rapid absorption took place, followed by a slow continued absorption called the *swelling increment*. The latter, not previously described, occurred at approx. the same rate for most liquids, continued indefinitely without cessation, was independent of the initial swelling and could be increased or diminished by external agents which do not influence the initial absorption. Therefore the increment was not a slow approach to a max. swelling but was a characteristic of the system. Swelling is the resultant of 2 simultaneous processes: (1) satn. of the rubber with liquid, which reaches a max. and stops, and (2) a slow uniform increase in swelling (the increment). A time-swelling curve is the sum of the satn. and increment curves, and may be expressed by 4 factors: the *swelling max.*, *swelling time*, *satn. equation* and *increment*. The increment was probably caused by a gradual depolymerization of disaggregation of the rubber by dissolved O, because (1) there was no relation between the increment and the swelling max. or mech. properties; (2) vulcanization diminished swelling; (3) it was greatly increased by adding to the liquid certain agents which accelerate depolymerization or disaggregation; and (4) it was increased by oxidizing agents and diminished by antioxidants or exclusion of O. The increment was, therefore, the result of an oxidation process. Data on the swelling maxima, swelling times and increments of a cured rubber-S mixt. in C<sub>6</sub>H<sub>6</sub>, PhMe, xylene,  $\psi$ -cumene, tetralin, dekalin, petr. ether, gasoline, paraffin oil, turpentine, cyclohexane, cyclohexyl acetate, methylhexalin, AmOAc, Et<sub>2</sub>O and glycerol are given. The swelling max. depended upon the chem. compn. of the liquid rather than on its phys. properties, e. g., all hydrocarbons had high swelling powers; cyclic hydrocarbons had a higher power than aliphatic hydrocarbons of similar mol. wt.; unsatn. increased the power; introduction of halogen increased the power; polar substituents lowered the power; esterification of an OH group increased the power; with the same polar group the higher the mol. wt. the higher the power; and in chem. similar liquids the higher the dielec. const. the lower the power. Mixts. of liquids had in most cases greater swelling capacities than those calcd. from the components. The swelling time depended chiefly upon the phys. properties, particularly the viscosity, the results indicating an approx. proportionality. There was no direct relation between swelling max. and swelling time, the initial rate of



absorption being proportional to the swelling max. divided by the swelling time. The initial rate was not, therefore, a measure of the swelling capacity. No relation was found between the increment and the chem. or phys. properties of the liquid. Swelling was influenced by the presence in the liquid of acids, bases, metal salts, oxidizing agents, antioxidants, vulcanizing agents and accelerators, the influence on the swelling max. and increment of Cu oleate, Mn oleate, AcOH,  $\text{ClCH}_2\text{CO}_2\text{H}$ ,  $\text{Cl}_3\text{CCO}_2\text{H}$ , oleic acid,  $\text{PhNH}_2$ , hydrazobenzene, piperidine,  $\text{C}_6\text{H}_5\text{N}$ , diphenylguanidine,  $p\text{-ONC}_6\text{H}_4\text{NMe}_2$ , piperidine-pentamethylenedithiocarbamate, tetramethylthiuramdisulfide,  $(\text{NH}_4)_2\text{CS}$ , Zn ethylxanthate, S,  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ , 2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{Me}$ , benzoyl peroxide, turpentine, pyrogallol, quinol, "Antox," rubber resin and water being tabulated. The increment was increased by acids, org. bases, Cu salts, Mn salts, oxidizing agents, accelerators and S, whereas antioxidants, rubber resins and water diminished it. Those substances which depolymerize, disaggregate or oxidize seemed to increase the increment, whereas those which retard oxidation diminished it. The swelling max. diminished with increased cure, i. e., with increased combined S; and the swelling time and increment appeared to change in the same way. The addn. of a non-swelling ingredient reduced the swelling process only in part because of the lowering of the rubber content, for by allowing for this lower % rubber it was found that fillers, particularly the reinforcing type, changed the properties of the rubber so that it swelled less readily. With a given % combined S, accelerators in the rubber reduced swelling, and the more active the accelerator the less was the swelling. In the rubber, antioxidants reduced the increment, but did not change the swelling max. greatly. During both natural and accelerated (Geer) aging, the swelling max. and the swelling time at first diminished, passed a min. and then increased, sometimes followed by a 2nd and final decrease. The changes in swelling closely resembled the changes in elongation under const. load. In natural aging the swelling increment changed but little, but in the Geer oven it did not behave in the same way. The swelling max. increased with increase in temp., indications being a coeff. of 1.03 per  $10^\circ$  near  $30^\circ$ , which means close proportionality with the abs. temp. The increment was more sensitive, vis., 2.5 per  $10^\circ$  rise, or roughly that of a chem. reaction, as would be expected if it resulted from depolymerization or disaggregation by O. Exposure to light increased the swelling increment, while the swelling max. was not affected. A survey of all data indicated that swelling max. is a property intermediate between elongation at const. load and hardness, more nearly resembling the latter, but that it bears no relation to tensile strength, resilience and permanent set. The increment was independent of the mech. properties, and though caused by atm. O, complications make it impossible to judge relative aging properties by relative increments. Swelling tests are of practical application in studies of oil-resisting rubber mixts., rates of vulcanization, antioxidants, deleterious substances, aging, etc. Attention is called to the danger of drawing conclusions on the relative swelling capacities of rubber mixts. or of liquids by only a short time of immersion, since the latter gives merely the initial rate of absorption, and this is no guide to the swelling capacity. In comparisons, swelling must be continued at least until the straight part of the time-swelling curve is reached. C. C. D.

**Relation between artificial aging tests and natural aging.** J. M. BIERER AND C. C. DAVIS. *Ind. Eng. Chem.* 21, 1008-9 (1929).—Most rubber goods deteriorate from several influences, and because no artificial aging test yet devised intensifies each factor to the same degree, there is at present no artificial duplication of natural aging. However, where the predominant effect is the same in natural aging and in the artificial test, the latter is of practical value. Sunlight plays a very important part in the aging of some products, and an artificial test to simulate this effect is badly needed. C. C. DAVIS

**Natural vs. artificial aging.** STANLEY KRALL. *Ind. Eng. Chem.* 21, 1009-12 (1929).—Comparative artificial and natural aging tests show no general relationship between the natural aging of 3 tire mixts. and their aging in the O bomb and in the Geer oven. The results also show the need of choosing an artificial test which approaches the conditions encountered in natural aging. C. C. DAVIS

**Correlation of various aging tests with natural shelf aging.** SIDNEY M. CADWELL. *Ind. Eng. Chem.* 21, 1017-9 (1929).—The diversity of conditions under which different rubber products age naturally makes the duplication of natural aging by any general artificial method impracticable. The Geer oven test and the O bomb test do, however, show in a qual. way distinctions between good and badly aging rubber mixts. Because no strictly quant. relations between natural aging and artificial aging tests have been established, from a practical point of view it is advisable to assure good aging by proper cures, the use of antioxidants and the avoidance of deleterious impurities. Tests of the aging of rubber-S (100-6.6) mixts. contg. various antioxidants and cured to different degrees show that the less the combined S the longer the life as judged by the O bomb test. C. C. DAVIS

**Accelerated aging vs. shelf aging.** EVERETT M. FOLLANSBEE. *Ind. Eng. Chem.*

21, 1012(1929).—Tests of rubber mixts. of various types show no const. time ratio between natural aging and aging in either the Geer oven or in the O bomb. C. C. D.

**Aging of mechanical rubber goods stocks by various methods.** K. J. SOULE. *Ind. Eng. Chem.* 21, 1013-5(1929).—Comparative tests of the aging of 30 mech. rubber goods mixts. in natural life, in the Geer oven and in the O bomb show no definite correlation between natural and artificial aging. There was no essential difference in the extent to which the Geer oven and the O bomb simulated natural aging. C. C. DAVIS

**Standardization of vulcanization testing.** J. R. SCOTT. *Trans. Inst. Rubber Industry* 5, 139-50(1929).—A crit. discussion of present methods of testing and the need of standardization. C. C. DAVIS

**The vulcanization of rubber goods of various colors and with different accelerators by the aid of ultra-violet light.** RUDOLF DITMAR AND K. H. PREUSSE. *Caoutchouc & gutta-percha* 26, 14762-3(1929).—A continuation of expts. which showed that with Se red and tetramethyl thiuramdisulfide brilliantly colored vulcanizates can be obtained after very short cures in ultra-violet light (cf. D. and Grünfeld, C. A. 23, 5612). Formulas of blue, green, orange, red and brown rubber mixts. which will cure in 7 min. at a distance of 10 cm. from the source of light are given. C. C. DAVIS

**Table of changes to be made in the time of vulcanization with the degrees of heat.** WERNER ESCH. *Gummi-Ztg.* 44, 361(1929).—The lower the temp. the longer the time necessary to reach a given state of cure. A table shows the factors by which to multiply any time of cure to obtain the longer time of cure for any lower temp. of cure. These values are based on a factor of 2 for each 7° reduction of temp., i. e., a cure 7° lower than another requires twice as long and a cure 14° lower than the original cure requires 4 times as long. The criterion of these similar states of cure is not mentioned. C. C. D.

**Health hazards in the rubber industry.** L. J. D. HEALY. *India Rubber World* 81, No. 3, 71-2(1929).—An investigation of the Health Standards Comm. of the Safety Council leads to the classifying of antioxidants and accelerators into 4 groups: (1) highly toxic or irritant, to be avoided or used with extreme caution; (2) moderately toxic or irritant, care to be used; (3) slightly toxic or irritant, no hazards with proper handling but hazardous with promiscuous handling and (4) relatively low toxicity, with no hazard by ordinary handling. A list shows 8, 20, 24 and 54 com. accelerators and antioxidants (some repeated by com. and chem. names) in the 4 groups. C. C. DAVIS

**Color reactions of rubber and gutta-percha.** F. KIRCHHOF. *Kautschuk* 5, 150(1929).—A previous article on the subject by K. (C. A. 23, 2068) leads to the question whether colored products of the fusion of phenols with hydrocarbon bromides give characteristic absorption spectra. When rubber bromide-phenol or gutta-percha bromide-phenol fusion mixts. are put in solvents, the stability of the colors depends upon the particular solvent. Examn. of the absorption spectra of a violet and of a yellow-brown soln. in  $\text{CHCl}_3$  showed almost the same absorption band between 490 and 540  $\mu$  and the yellow-brown soln. showed the greater extinction of the blue-violet part. This agrees with the color-degree of the dispersion rule for colloid solns. The colloidal nature of colored hydroxyphenyl rubber solns. is further substantiated by strong Tyndall effects and by filtering, in the latter case, blue and yellow solns. passing completely and violet and brown solns. leaving unfilterable residues. Therefore, the violet and brown colors originate from blue and violet solns. by increase in particle size. Yellow solns. (partially mol.) are formed from violet solns. by diminution of particle size. There may be other deep-seated causes of the colors. C. C. DAVIS

**Increases in temperature in rubber-fabric belts during operation.** H. BRANDT. *Kautschuk* 5, 250-5(1929). C. C. DAVIS

**The value of reclaim.** HENRY P. STEVENS. *Bull. Rubber Growers' Assoc.* 11, 762-3(1929).—Comments on an article by Sanderson (cf. C. A. 23, 4099). C. C. D.

**Influence of pigments on some physical properties of unvulcanized rubber.** HARLAN A. DEFEW. *Ind. Eng. Chem.* 21, 1027-30(1929).—The "soly." of raw rubber contg. fine pigments in  $\text{C}_6\text{H}_6$  can be increased by changing the interfacial energy between rubber and pigment, a change which can be brought about in either of 2 ways: (1) by changing the condition of the rubber, e. g., by further mastication, or (2) by changing the condition of the surface of the pigment, e. g., if it is  $\text{ZnO}$  by treatment with  $\text{SO}_2$ , which forms a coating of  $\text{ZnSO}_4$ . Pigments render rubber insol. in org. solvents probably because the flocculated portion of the pigment (cf. C. A. 23, 2068) acts as a semi-permeable membrane, holding back the rubber. If so, the higher the concn. of a given pigment, the lower the soly. of a given mixt. and the smaller the size of the units of the aggregated rubber the greater the soly. of the mixt. Expts. confirm both these assumptions, though in the 2nd case improved dispersion may also be responsible. On storage soly. diminishes, perhaps because of a change in the structure or condition of the rubber or of the protein. The theory of Stevens (cf. C. A. 21, 1703) may be the explanation of

the insoly. of vulcanized rubber. Tests show that the alky. of ZnO plays no part in the soly. phenomena of rubber mixts. contg. ZnO.

C. C. DAVIS

**Structural differences in masticated and unmasticated raw rubber mixtures and vulcanizates and their significance from a practical point of view.** E. A. HAUSER WITH M. HUNEMÖRDER. *Kautschuk* 5, 151-2(1929).—Microscopic examn. of smoked sheet shows the absence of any structure optically. After digestion in water, however, the original structure of the closely packed latex particles became visible. This is explained by the layer of resin and protein (which is strongly adsorbed on the rubber) swelling so much that the  $n$  value of the adsorbed layer becomes enough different from that of the rubber to make the interface visible. If smoked sheet in progressively increasing stages of mastication is digested in water, the visible structure disappears with increasing mastication, because of the progressive destruction of the particles. Vulcanization does not alter these optical phenomena. Vulcanizates prepd. from latex without mastication of the rubber show much greater resistance to tear than vulcanizates from masticated rubber. There is no generally satisfactory theory to account for the different effects of diluent and reënforcing fillers, but this difference can be shown strikingly by expt. Microscopically, diluent fillers, e. g., barytes, show on stretching the rubber a loosening and sepn. from the rubber, with formation of vacuoles contg. the free mineral particles. Here tearing proceeds at the interface of filler and rubber. With reënforcing fillers, the high interfacial adhesion is greater than the cohesion of the rubber, so tearing occurs through the rubber matrix. With loaded latex mixts. the tearing depends less upon the interfacial adhesion, for the adsorption forces between latex and filler particles also play a part, and so tearing is also a function of the relative surface areas of rubber and filler particles. If loading is so great that all the surface of the rubber is occupied by filler, then tearing proceeds easily by disintegration of the filler medium. This means in turn that the proportions of reënforcing filler which give the best quality in vulcanizates from masticated rubber may be different from those giving the best quality in vulcanizates from latex. Exptl. evidence now shows the superiority of products made from latex, and progress in the direct use of latex is far enough advanced to indicate great possibilities in the future.

C. C. DAVIS

**Vulcanization accelerators and their use. I. A survey of the present status of acceleration.** FRIEDRICH EMDEN. *Kautschuk* 5, 242-4(1929).—A discussion, with a table of 99 com. accelerators, their trade names, their chem. constitutions and the manufacturers.

C. C. DAVIS

**Vulcanization and the structure of rubber.** Answer to H. Loewen. EUGENIO LINDMAYER. *Kautschuk* 5, 202-4(1929).—Comments on an article by Loewen (cf. C. A. 23, 3373).

C. C. DAVIS

**Vulcanization of rubber by organic peroxides or by ammonium persulfate.** IVAN OSTROMUISLENSKII. *India Rubber World* 81, No. 3, 55-7(1929); cf. C. A. 23, 4847.—It was shown by O. in 1915 that rubber can be vulcanized by various org. peroxides in the absence of S and metallic oxides or accelerators. With 10-30% benzoyl peroxide the vulcanizates are soft and elastic and their phys. properties are not essentially different from those obtained with S or  $S_2Cl_2$ , and without other ingredients are transparent and almost colorless. These latter properties are the reason for the potential value of these vulcanizates. With 30% benzoyl peroxide cures are effected in 2 min. at 119°. Below 10% benzoyl peroxide (on the rubber) the vulcanizates are weak and tacky and even plastic. On aging these vulcanizates, even with the high proportions of benzoyl peroxide, change gradually to sticky viscous masses. S in such mixts. (0.2-1.0%) protects them from this oxidation and deterioration, but it renders them opaque. With higher proportions of S, e. g., a mixt. of rubber 100, S 10, benzoyl peroxide 10, white vulcanizates with high tensile strengths are obtained at short cures, viz., 25 min. at 13 lb. per sq. in. steam pressure. On the other hand Se, Te, their sulfides, metallic oxides (particularly PbO), amines, tannic acid and powder. Al accelerate the deterioration. Compared with S, benzoyl peroxide is so active that in mixts. contg. both, the latter is the predominant vulcanizing agent. When, however, rubber mixts. contg. certain nitrobenzenes and benzoyl peroxide are vulcanized, the latter remains passive and vulcanization is effected solely by the nitrobenzene.  $NH_4$  persulfate vulcanizes rubber in a normal fashion except that the products are porous because of evolution of a gas, perhaps  $NH_3$  or  $SO_2$ .

C. C. DAVIS

**The question of vulcanization without sulfur. Experiments on hot vulcanization and vulcanization in ultra-violet light with the aid of trinitrobenzene and trinitrophenol.** F. KIRCHHOF. *Gummi-Ztg.* 44, 252-3(1929).—The expts. which are described indicate that neither 2,4,6-trinitrobenzene (I) nor picric acid (II) is an effective vulcanizing agent in the absence of S. This finding is in great contrast to the work of Ostromuislenskii (cf. C. A. 23, 4847) which attempts to show the excellent cures which may be obtained with these substances. A mixt. of brown crepe 100, PbO 30, II 0.5 would not cure at



140°, but the same mixt. plus gas black 25 cured fairly well after 120 min. at 140°, showing that gas black has an activating effect. But even the best of the vulcanizates were leathery and inelastic and resembled S-vulcanizates only in that they had become insol. in  $C_6H_6$ . Since this absence of swelling is not in itself a satisfactory criterion of curing (uncured reclaimed rubber may not swell), the products can hardly be called "vulcanizates," but at best only "pseudo-vulcanizates." The 3 mixts.: (1) rubber 100, I 1; (2) rubber 100, PbO 30, I 1; (3) rubber 100, gas black 30, I 1 and (4) rubber 100, PbO 15, gas black 15, I 1, in the form of evapd.  $C_6H_6$  solns. were heated 30, 60 and 120 min. at 140°. (1), (2) and (3) did not vulcanize at all, and (4) only slightly. (2) showed evidence of depolymerization, as with rubber, PbO and II, proving that PbO is not an accelerator with I and II as with S. The changes in rubber observed by Ostro-muiskenskii are the type of transformation brought about by  $H_2SO_4$ , sulfo-acids, etc., and are also evident in reversion, overcure and reclaiming. Evapd. films from  $C_6H_6$  solns. of rubber-I and of rubber-II were exposed to ultra-violet light both in the open and hermetically sealed under quartz. Rubber contg. either I or II showed evidences of vulcanization, as indicated by loss of tackiness, and increase in elasticity and extensibility. There was a more pronounced change in the rubber-I mixts. than in the rubber-II mixts., and this conforms to the fact that when vulcanization in ultra-violet light takes place in the presence of II only the surface becomes vulcanized because the unvulcanized mixt., which is transparent to ultra-violet light, changes through isomerization of the rubber to an opaque medium, preventing further internal vulcanization. The results in general indicate that the products obtained by heating rubber with I or II and gas black resemble reclaim rubber and certain cyclo-rubbers physically and perhaps also chemically, and therefore are only "pseudo-vulcanizates." The vulcanizates obtained by the action of ultra-violet light are essentially different, particularly those with I, for physically and chemically they resemble "cold-cured" rubber.

C. C. DAVIS

**The preservation of rubber. The action of reducing agents.** GUSTAVE BERNSTEIN. *Mon. prod. chim.* 11, No. 110, 1-4; *Chem. Zentr.* 1928, II, 819.—Depolymerized rubber is protected against oxidation by the addn. of reducing agents, like tannin (in vulcanization below 130°) or hydroquinone, which also act as protective agents in normal vulcanized material.

G. SCHWOCH

**The aging of rubber.** J. LAGERQUIST. *Tek. Tid., Uppl. C* 59, 34-40(1929).—A review accompanied by 98 literature references.

C. A. ROBAC

**The aging of vulcanized rubber under varying elongation.** A. A. SOMERVILLE, J. M. BALL AND W. H. COPE. *Ind. Eng. Chem.* 21, 1183-7(1929).—The expts. deal with the relative degree or rate of deterioration of various types of vulcanizates elongated statically to varying degrees and aged: (1) in the 70° air oven; (2) in the high-pressure O bomb; (3) in air contg.  $O_3$  and (4) outdoors (sunlight). The results, which are recorded in graphical form, admit of certain conclusions. Deterioration in the 70° air oven is about 30% greater at 100% elongation than at 0% elongation, whereas deterioration in the O bomb is almost independent of elongation. Deterioration in  $O_3$  and in sunlight is greatest at elongations of 5 and 10%. Cracking occurs in  $O_3$  and in sunlight when rubber is stretched, and in the air oven and O bomb, the greatest cracking is obtained at 5 and 10% elongations. The higher the total S content of a mixt. the more rapid is its deterioration in  $O_3$  and in sunlight. When a mixt. is undercured, it deteriorates more rapidly in  $O_3$  and in sunlight than does the same mixt. cured to its optimum condition. The addn. of a filler like whiting does not have any particular influence on the deterioration under the various conditions. Rubber bands showed progressively poorer aging in the O bomb as the elongation increased from 0 to 700%, while in air contg.  $O_3$  their aging was most rapid at 10% elongation and best at 400% elongation. Rubber cured with tetramethylthiuram disulfide (but no S) has particularly good aging properties and the aging is relatively insensitive to varying elongation. At the crit. 10% elongation, a high proportion of "mineral rubber" imparted better aging than a low proportion. Paraffin is a protective agent against sunlight but not against  $O_3$ . Two anti-oxidants may give similar results in oven and O bomb but different results in sunlight and in ozonized air. Synthetic rubber behaves like natural rubber when aged in air contg.  $O_3$ .

C. C. DAVIS

**Permeability of rubber to air. I. Effect of temperature, pressure and humidity.** V. N. MORRIS AND J. N. STREET. *Ind. Eng. Chem.* 21, 1215-9(1929).—The subject has become of importance for inner tubes, airships, gas masks, tennis balls, etc. An app., termed a *permeameter* (measuring the vol. of gas passing), and the technic for studying the influence of heat, pressure of the confined air and moisture content of the rubber on the permeability of the rubber are described and illustrated. The results show that under the conditions of the expts. the permeability is almost linearly proportional to the total pressure. The *temp. coeff. of the permeability* was very high (e. g., a drop of 20°F. cutting the permeability to about 0.5 its value, and the permeability being extremely

low at 0° C.), which is of great practical interest with inner tubes. Moisture in the rubber had a tendency to diminish the permeability to a slight degree. When, however, the rubber had undergone prolonged immersion in water, the permeability was higher than in the dry state.

C. C. DAVIS

**Preparation of reclaimed rubber with soy-bean oil.** YOSHIHIDE KAKIMOTO. *Repts. Osaka Ind. Research Inst. Japan* 19, No. 9 (1929).—The method of prepreg. reclaimed rubber with soy-bean oil under various conditions was studied. The material was prepreg. by vulcanizing F. A. Q. smoked sheet with acid-free S (90:10 ratio) under proper conditions. Reclaimed rubber was prepreg. by the usual method, i. e., by mixing the vulcanizate with soy-bean oil. The mixt. of vulcanizate and oil was vulcanized with S (60:30:10 ratio) under various conditions. The best quality was obtained when the prepreg. was carried out at a steam pressure of 90 lb. per sq. in. for 9 hrs. A small proportion of moisture in the vulcanizate did not affect the quality of reclaimed rubber. The better quality was also obtained by using very small granules of vulcanizate and about 20% of soy-bean oil.

F. I. NAKAMURA

**Quality control of reclaimed rubber.** WEBSTER NORRIS. *India Rubber World* 81, No. 4, 55-6 (1930).—A discussion of methods of controlling mfg. operations, scrap selection, d., rubber content and quality before and after curing.

C. C. DAVIS

**The use of improved oils for the preparation of factice.** L. AUER. *Kautschuk* 5, 153-6 (1929).—Further data are presented to show the results obtained under different conditions in the use of the new type of factice already described in detail (cf. C. A. 23, 4370).

C. C. DAVIS

**Vulcanization accelerators of the mercaptobenzothiazole series.** J. ALTPETER. *Metallbörse* 19, 2583, 2639 (1929).—A review with bibliography of American, Canadian and British patents.

W. C. EBAUGH

**Increase in the extensibility of dipped rubber goods and a reduction in the number of times of dipping of thick-walled dipped goods by increasing the viscosity of rubber solutions through the addition of Sipalin.** RUDOLF DITMAR AND KARL H. PREUSSE. *Chem.-Ztg.* 53, 779 (1929); cf. C. A. 22, 3065.—Tests of the elongation at rupture of balloons made by dipping and curing in  $S_2Cl_2$  soln. showed that methylcyclohexyl-methyladipate (Sipalin MOM) (I) increased the elongation at rupture greatly. Isopropyl methyladipate (Sipalin MOJ) (II) had little effect and methylcyclohexyl adipate (Sipalin AOM) (III) had none. Cured in  $S_2Cl_2$  vapor I increased the elongation greatly, III considerably and II a little. With the same dipping operation, a mixt. contg. S and accelerator and cured in hot air had the greatest elongation when III had been added. Here I had no influence and with II the elongation was lower than without any softener. I, II and III increased the viscosity of the solns. and allowed the dipping to be reduced considerably, e. g., from 8 to 5 dippings. In this respect III is the most effective.

C. C. DAVIS

**Rubber cements.** S. D. SUTTON. *India Rubber World* 81, No. 4, 59-60, 64 (1930); cf. C. A. 23, 5612 (1929).—The use of tire repair, boot and shoe, latex, rubber sole, flooring, garment and tennis ball cements is described.

C. C. DAVIS

**Fabrics used in rubber belting.** W. L. STURTEVANT AND J. E. SKANE. *India Rubber World* 81, No. 4, 65-8 (1930).—An illustrated description of the construction, properties, inspection and testing of different types of fabrics commonly used in rubber belting.

C. C. DAVIS

**Manufacture of tire treads.** JOSEPH ROSSMAN. *India Rubber World* 81, No. 4, 61-2 (1930).—A survey of U. S. patents relating to processes and machinery.

C. C. D.

**Rubber in airplane construction.** C. SAURER. *India Rubber World* 81, No. 4, 57-8 (1930).—An illustrated description.

C. C. DAVIS

**The rational utilization of scrap and reclaimed rubber.** The manufacture of hose. H. BAUFARON. *Déchets et régénérés* 1, No. 5, 3-5 (1929); cf. C. A. 24, 525.—Twelve rubber mixts. contg. reclaimed rubber for use in hose are given to show that for relatively cheap mixts. reclaimed rubber is a necessary ingredient to obtain the max. economy.

C. C. DAVIS

**New processes and equipment in the preparation of rubber.** N. H. VAN HARPEN. *Arch. Rubbercultuur* 13, 609-34 (1929). (In English 635-51).—A discussion with illustrations, dealing with anti-coagulants, the straining of latex, anti-mold prepps., bacterial rust, safety devices,  $Na_2SiF_6$  as a coagulant, the machining of crepe rubber and drying sheds with artificial heating.

C. C. DAVIS

**The preparation of rubber mixtures.** M. L. P. *Rev. gén. caoutchouc* 6, No. 56, 3-8 (1929).—A general discussion, with diagrams and description of mill systems, and methods and cooling equipment for mills.

C. C. DAVIS

**The manufacture of rubber rolls.** I. L. FÜLLSACK. *Gummi-Ztg.* 44, 523-4 (1929).—Descriptive.

C. C. DAVIS

The manufacture of rubber rolls. II. L. FÜLLSACK. *Gummi-Ztg.* 44, 634, 636-7 (1929); cf. preceding abstr.—A further discussion. C. C. DAVIS

Suggestions for the standardization of rubberized fabric, particularly wearing apparel (mantling). WERNER ESCH. *Gummi-Ztg.* 44, 470, 472-3 (1929).—Formulas and methods are discussed. C. C. DAVIS

Suggestions for the standardization for rubberized fabrics, particularly wearing apparel (mantling). ANON. *Gummi-Ztg.* 44, 637 (1929).—Comments on an article by Esch (cf. preceding abstr.). Reply. WERNER ESCH. *Ibid* 637-8. Further comments. ERNST ADEL. *Ibid* 638, 640. C. C. DAVIS

Manufacture of ebonite sheets for use in the wireless telegraph industry. FRANK A. BATH. *Rev. gén. caoutchouc* 6, No. 56, 9-12 (1929); cf. B. and Fraser, *C. A.* 24, 264.—The subjects which are discussed include calendered sheets with grained, marbled and engraved surfaces, polishing and cutting. C. C. DAVIS

An attempt at a rational classification of the principal accelerators of vulcanization. II. A study of the time required for vulcanization to give the maximum physical properties at different temperatures. R. THIOLLET AND G. MARTIN. *Caoutchouc & gutta-percha* 26, 14722-30 (1929); cf. M. and T., *C. A.* 23, 4101.—The new expts. deal with (1) the time of vulcanization at a given temp. required to obtain the optimum phys. properties (max. tensile strength), and (2) the temp. of cure which gives the optimum phys. properties. The same base mixt. and the same accelerators were used as before. Graphs in which the ordinates are times of vulcanization and the abscissas the tensile strengths and elongations show the characteristics of the various accelerators. The temp. at which the max. tensile strength occurs is called the *characteristic temp.* of the accelerator. The accelerators were classified according to the time required to attain the optimum phys. properties when vulcanization was at the characteristic temp. The following data give for each accelerator the characteristic temp. (as steam pressure in kg. per sq. in.) and the time (in min.) at this temp. to reach the optimum quality, resp.: thiocarbamilide 3, 110; anhydroformaldehyde-aniline 3, 90; triphenylguanidine 3, 85; phenyltolylxylylguanidine 3, 80; *p*-nitrosodimethylaniline 2.5, 75; anhydroformaldehyde-*p*-toluidine + diphenylguanidine 3, 75; di-*o*-tolylguanidine 3, 70; ethylidene-aniline 2.5, 50; mercaptobenzothiazole 3, 45; mercaptobenzothiazole + diphenylguanidine 1.5, 40; Zn methylphenyldithiocarbamate 0.75, 30; mercaptobenzothiazole + ethylidene-aniline 2, 25; tetramethylthiuram disulfide 2, 10. These data show the most favorable combination of time and temp. for each accelerator. By the joint use of a 2nd accelerator it is possible to retard the precocity of certain accelerators, and in some cases this 2nd accelerator does not influence the subsequent course of vulcanization, the max. tensile strength being obtained at the same time of heating. This means that rapid accelerators can be made easier to handle without diminishing their activity. Besides this benefit, the plateau of vulcanization with a given accelerator may be extended by the joint use of another accelerator so that overcuring dangers are minimized and more uniform quality in practice is obtained. Tests with xanthates show that at 100° the optimum phys. properties are reached rapidly and this quality is maintained when the cure is continued, in consequence of the destruction of accelerator. Here, then, the state of cure can be controlled only by the proportion of accelerator. For curing in hot air, it may be desirable to use double acceleration, a precocious accelerator to effect rapid fixation and a 2nd accelerator to reach the optimum properties as soon as practicable. For curing large masses, uniform curing may be obtained: (1) with an accelerator which is inactive at low temps. so that vulcanization begins only when the mass has become uniformly hot or (2) with a precocious accelerator having a broad plateau of vulcanization, thus allowing prolonged heating of the outer portions. Particular com. accelerators are cited in the paper as examples of the various points discussed. C. C. DAVIS

The rubber industry in 1929. S. A. BRAZIER. *Ind. Chemist* 6, 30-4 (1930). E. H.

A study of the effect of damp storage on raw rubber. B. J. EATON AND R. G. FULLERTON. *Rubber Research Inst. Malaya Bull.* 2, Oct., 1929, 26 pp.—The work includes various aspects, including the effects of molds on smoked and on air-dried sheet not treated with a sp. fungicide, on smoked and on air-dried sheet treated with a sp. fungicide, the effect of "spot disease" on thin pale crepe, the effect of molds on the N content of rubber, the fungicidal value of *p*-nitrophenol and  $\text{Cl}_2\text{C}_6\text{H}_3\text{ONa}$ , and the development of white or virgin streak in smoked sheet. When allowed to absorb moisture, smoked sheet and air-dried sheet almost always develop molds from spores which enter the latex after it exudes from the tree, or which enter the coagulum at some stage during its prepn. When raw rubber is stored in air with high humidity, the absorption of moisture reaches a max. after a few days. In rubber in which molds develop, there is a loss of wt. which increases progressively for a long period; in one case a loss of 17%

during 15 months of damp storage was noted. The loss of wt. by the action of molds shows that the rubber hydrocarbon is attacked, for the highest grade of rubber does not contain over 5-6% non-rubber components. Since none of the samples was rewashed or treated with any solvent, these losses were in gaseous form. When sheet is well smoked, molds develop only after long periods. The addn. of *p*-nitrophenol to latex, or the subsequent treatment of the fresh sheet with dil. *p*-nitrophenol, retards considerably, though it does not prevent, the growth of molds. In practice  $\text{Cl}_3\text{C}_6\text{H}_2\text{ONa}$  is not so effective as *p*-nitrophenol as an inhibitor of mold growth, because the dil. acid used as a coagulant converts it into highly volatile  $\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$ . The development of chromogenic organisms in crepe in damp storage also causes a loss of wt., though the losses are smaller than with sheet. The growth of molds causes no loss of N, though the N components may be changed in character. The development of a defect in smoked sheet known as "white" or "virgin streak" is caused by allowing the rubber to become damp, and is not a result of insufficient drying during the smoking process. When allowed to become damp, dry unsmoked rubber becomes white and opaque throughout. In smoke-drying rubber, as carried out in recent yrs., the wood fuel is burned too thoroughly, so that a smoke is produced which contains too little creosote and other antiseptics. This, however, concerns only the effect of smoking on the development of mold, and not the effect of smoking on the quality of rubber. Further investigations of the smoking process and different treatments of rubber with *p*-nitrophenol and other fungicides are necessary before definite recommendations for a procedure can be given. C. C. D.

**The relation between stresses and deformations, with special reference to rubber.** RAFFAELE ARIANO. *Nuovo Cimento* [N. S.], 6, 123-56(1929); cf. C. A. 23, 545.—An analysis of the relations between the various possible types of deformation in raw and vulcanized rubber indicate that these materials parallel to some extent the behavior of metallic substances. Modern theories of the structure of raw rubber are reviewed and the deformations of vulcanized rubber subjected to crit. analysis. L. T. FAIRHALL

**Defects in smoked sheet and crepe rubber.** R. G. FULLERTON. *Rubber Research Inst. Malaya Quart. J.* 1, No. 1-2, 66-74(1929).—A description of the nature and characteristics of common defects in smoked sheet and crepe and a discussion of the principles of estate methods used for the prevention of these defects. The chief defects in smoked sheet are mold, bubbles and rust, and in crepe, "spot disease," tackiness and yellow discoloration. Most of the defects (except tackiness) found today in plantation rubber have no effect on the quality of the vulcanized rubber, and the only objection is the unsightly appearance. Besides adequate smoking *p*-nitrophenol is a satisfactory antiseptic, either added to the latex or used in soln. for soaking the rubber. Bubbles (large or microscopic) are nearly always the result of fermentation, and can be prevented by the addn. of  $\text{Na}_2\text{SO}_3$  to the latex. Rust is composed of decompn. products of serum substances from the action of microorganisms. Moisture favors its formation and it can be prevented or minimized by rapid drying of the sheet. *p*-Nitrophenol prevents rust as it does molding. "Spot disease" (of various colors) in crepe results from the growth of fungi, is favored by air, warmth and moisture, and can be prevented by minimizing exposure to dampness during the operations, avoiding an excess or deficiency of  $\text{NaHSO}_3$ , etc., or in addn. by digesting the fresh crepe in 1% aq.  $\text{HCHO}$ . Tackiness, rare in high-grade crepe, can be detrimental to quality; it may be caused by microorganisms, exposure to sunlight or heat, excessive mastication or Cu. Yellow crepe contains a yellow pigment which occurs naturally under some conditions, e. g., during new tapping. It can be removed only by fractional coagulation. C. C. DAVIS

**Rationalization of rubber mixtures by the use of coal ash as a filler.** RUDOLF DITMAR. *Caoutchouc & gutta-percha* 26, 14804-6(1929).—Tests are described which show that coal ash may be an economical filler in certain types of rubber mixts. (cf. Marter, Brit. Pat. 1843, C. A. 7, 2486). It should not have an acid reaction, should be free of Cu and Mn and should be colloidal rather than cryst. C. C. DAVIS

**Estimation of the degree of penetration of rubber into fabrics.** E. O. DIETERICH. *Ind. Eng. Chem., Anal. Ed.* 2, 102-3(1930).—The rubber is cured to hard (not brittle) rubber by heating 12-15 hrs. at a convenient curing temp., e. g., 300°F., in satd. aq. Na or Ca polysulfide contg. excess S and preferably also a water-sol. accelerator. The product is washed, dried and sectioned to 0.05-0.10 mm. with a microtome; the sections are digested in concd.  $\text{H}_2\text{SO}_4$ , until all cotton has disappeared, washed with concd.  $\text{H}_2\text{SO}_4$ , mounted in the latter and examd. or photographed microscopically. Typical results are illustrated. C. C. DAVIS

**Rubber as a substitute for leather.** PHILIP SCHIDROWITZ. *Trans. Inst. Rubber Industry* 5, 207-18(1929).—An extensive discussion dealing with the comparative advantages and disadvantages of rubber and leather, developments in the use of rubber products in place of those of leather, leather-like rubber products, top stocks, uppers, automobile hoods, etc. A general discussion follows the paper. C. C. DAVIS



**Rubber soles for footwear.** F. JACOBS. *Caoutchouc & gutta-percha* 26, 14806, 14807-8, 14809-10, 14811(1929).—An illustrated description, dealing with the general features of manuf. C. C. DAVIS

**Flexing test for tire carcass stocks.** W. A. GIBBONS. *Ind. Eng. Chem., Anal. Ed.* 2, 99-102(1930).—Though the test which is described, with representative data obtained, does not give direct evidence of the wearing life of a tire, it is useful in studying the effects of compounding ingredients, aging, impregnation of fabric, calendering, curing, etc. C. C. DAVIS

**The accelerating influence of a basic azo dye in vulcanization.** T. J. DRAKELEY AND A. G. COUISON. *Trans. Inst. Rubber Industry* 5, 179-83(1929).—Expts. show that Bismarck brown has a marked accelerating action in various types of rubber mixts.; so when this dye is used for coloring rubber mixts. shorter times of cure may be practicable. Compared, however, with the activity of ordinary com. accelerators, this action is feeble; so when diphenylguanidine is used simultaneously the latter masks to a great extent the effect of the Bismarck brown. C. C. DAVIS

**Comparison of various organic reagents for accelerating vulcanization of rubber.** YUTAKA TANAKA AND GIHEI HARA. *Bull. Osaka Inst. Ind. Res. (Japan)* [1], 10, 1-29 (1929).—Eighty-eight substances were tested, the mixts. were made as near as possible like those in actual practice. The accelerators, their proportion in the mixts., and the time of vulcanization were varied. The breaking strength, hardness, elasticity and combined S were detd. to ascertain the effect of the proportion of added S and of the accelerators. The order of accelerating action, and the suitable % to be used (based on the rubber) were as follows: *piperidylpentamethylenedithiocarbamate*, 0.25-0.5; *p-nitrodimethylaniline*, 0.25-1.0; *diphenylguanidine*, 0.5-2.0; *p-phenylenediamine*, 0.5-3.0; *hexamethylenetetramine*, 0.5-4.0; *triphenylguanidine*, 0.5-4.0; *aldehyde-ammonia*, 0.75-4.0; *thiocarbamilide*, 1.0-4.0. The effect of the accelerator differed with the added S and with the particular accelerator, so that these factors must be regulated suitably. The breaking strength, elongation, hardness and elasticity varied markedly with the kind of accelerator, so that attempts at shortening the time of vulcanization by merely adding these accelerators to mixts., the compn. of which is suitable for some products already in the market, is liable to fail, especially in such articles as those in which the feeling as judged by touch is important. The extent of shortening of the time of vulcanization is relatively large when the quantity of added reagent is small, and when it is large as often in actual practice there is no such marked shortening effect. By the suitable use of org. accelerators, the S may be decreased up to the limit of 1% on the raw rubber. K. SOMEYA

**Vulcanization experiments with aniline sulfate.** A. ZEITLIN AND L. H. WILLIAMS. *Trans. Inst. Rubber Industry* 5, 173-8(1929).—The expts. are part of an investigation of the comparative accelerating effects of simple aromatic amines, and deal with the accelerating action of aniline sulfate. The 2 mixts. (1) pale crepe 100, S 10 and (2) pale crepe 100, S 10, aniline sulfate 4, vulcanized at the same rate and gave vulcanizates of approx. the same quality; so in rubber-S mixts. aniline sulfate behaves as an inert filler. Aniline sulfate retarded the rate of vulcanization of the mixt.: pale crepe 100, S 10, PbO 10. In the rubber-S mixts. aniline sulfate did not decompose at the temps. of vulcanization, and with PbO present, it decomposed only partially; so no quant. relations between the retardation and the decompn. of the aniline sulfate could be adduced. C. C. DAVIS

**The question of vulcanization without sulfur. Experiments on hot vulcanization in ultra-violet light with the aid of 1,3,5-trinitrobenzene in picric acid.** F. KIRCHHOF. *Rubber Age* (N. Y.) 26, 377-8(1930).—English translation (cf. *C. A.* 24, 750). C. C. DAVIS

## Patents

**Rubber.** THE NAUGATUCK CHEM. CO. Fr. 660,491, Sept. 15, 1928. A reversible gel of non-coagulated latex is obtained by treating the latex by incorporation of a hydrosol of  $H_2SiO_2$  and allowing the latex to rest until the formation of a gel. The hydrosol may be formed in the latex by adding a silicate thereto and treating with a dil. acid such as boric acid.

**Rubber latex.** ÉDUARD S. ALI-COHEN. Fr. 661,178, Sept. 28, 1928. A rubber latex which is non-hygroscopic and which can be used as gutta-percha is prepd. by mixing with the latex an emulsion or a chem. combination of one or more resins, one or more waxes or a mixt. of resins or waxes with a soln. of soap, after which the mixt. is coagulated by adding an Al salt, e. g.,  $Al_2(SO_4)_3$  or an alum.

**Electroösmotic separation of rubber particles from latex, etc.** SIEMENS-ELEKTRO-

**OSMOSE GES.** Brit. 307,912, March 17, 1928. Latex or the like which is to be treated by the process described in Brit. 305,630 (C. A. 23, 4628) is preliminarily treated with a weakly acid gas or gaseous mixt. such as  $\text{CO}_2$  to reduce its  $p_H$  to 7 or less. Ammoniacal latex may be first heated to expel  $\text{NH}_3$  in part.

**Dispersing rubber in water.** WILLIAM B. PRATT (to Dispersion Process, Inc.). U. S. 1,731,725, Oct. 15. A coagulated rubber mass is dispersed in water with the aid of a dispersing agent such as colloidal clay, which affords a protecting coating for the dispersed particles; a flocculating agent is then incorporated in the product in sufficient quantity to permit the dispersed rubber product to be spread in a layer which is tacky, coherent and irreversible when dry.

**Aqueous rubber dispersion.** WILLIAM B. PRATT (to Dispersion Process, Inc.). U. S. 1,732,027, Oct. 15. In forming an aq. dispersion of coagulated rubber, there is incorporated into a coherent mass of rubber a colloidal dispersing agent such as glue; the mass is subjected to stretching in the presence of water, with absorption of water, until the rubber mass seps. and disperses in globular form in the water. A product is obtained having characteristics resembling those of latex.

**Rubber compositions.** WILLIAM C. GEER (to B. F. Goodrich Co.). U. S. 1,731,484, Oct. 15. Comps. which are suitable for elec. insulation are formed of uncured rubber together with a hard, tough, non-grindable thermoplastic reaction product of rubber and a sulfonic acid such as phenolsulfonic acid or the like.

**Rubber compositions.** WILLIAM C. GEER and HARRY L. FISHER (to B. F. Goodrich Co.). U. S. 1,731,485, Oct. 15. By the reaction of rubber with *p*-toluenesulfonic acid or the like, products are obtained which are suitable for use in marine cable insulation, etc.

**Rubber compositions.** WILLIAM C. GEER and HARRY L. FISHER (to B. F. Goodrich Co.). U. S. 1,731,849, Oct. 15. A rubber compn. having a low moisture absorption is produced by effecting a reaction between rubber and phenolsulfonic acid or other suitable acid reagent contg. the grouping  $\text{R-SO}_3\text{-X}$  in which R represents an org. radical or a hydroxy group and X represents Cl or a hydroxy group, and mixing with the product a material such as a wax or oil having a low water-absorption capacity to modify the plasticity of the substance. The product is suitable for elec. insulation, etc.

**Rubber composition for making sound records, etc.** HARRY L. FISHER and WILLIAM C. GEER (to B. F. Goodrich Co.). U. S. 1,731,483, Oct. 15. Infusorial earth 100-250, Fe oxide 100-300, gas black 10-50, cotton flock 10-50 and a softener such as paraffin, stearic acid or palm oil 10-50 parts are mixed with 300 parts of a hard, friable, thermoplastic deriv. of rubber, which may be formed by the action of *p*-toluenesulfonic acid and  $\text{H}_2\text{SO}_4$  on rubber.

**Rubber composition suitable for electrical insulation.** WILLIAM C. GEER (to B. F. Goodrich Co.). U. S. 1,731,487, Oct. 15. Comps. which are suitable for cable insulation are formed from a mixt. of (a) unvulcanized rubber, (b) a hard exothermal reaction product of rubber such as that formed with pine tar and  $\text{H}_2\text{SO}_4$ , and (c) a masticated vulcanized rubber with which, before vulcanization, there is admixed a tough, non-friable reaction product of rubber and a sulfonic acid, e. g., *p*-toluenesulfonic acid. The ingredients are intimately mixed to form a solid suspension. Cf. C. A. 23, 3828.

**Rubber electrical insulation.** BELL TELEPHONE LABORATORIES, INC. Brit. 307,966, Dec. 15, 1927. A product of very low N content and good insulating properties is obtained by treating crude rubber with water at a high temp. (suitably at  $150^\circ$  for 24 hrs.) and then washing or by heating dild. latex to a high temp. (suitably  $150^\circ$  for 13 hrs.) and then coagulating and washing. Balata and gutta-percha may be similarly treated to reduce their N content, and various mixts. of treated rubber, montan wax or the like, balata and gutta-percha may be used for insulation.

**Electrodeposition of rubber.** SIEMENS & HALSKE A.-G. Brit. 307,747, March 12, 1928. Deposition from a rubber suspension or latex is effected by use of a. c., the frequency of which may be up to 150. Electrodes of Al or Ta are preferred and these are preferably covered with a porous non-conducting or "semi-conducting" material such as plaster of Paris or a metal oxide. With such coverings, electrodes of Fe or Pb also may be used. Various details of operation are given.

**Electrodeposition of rubber, etc.** SIEMENS-ELEKTRO-OSMOSE GES. Brit. 307,879, March 15, 1928. Particles are sepd. from a suspension by electroosmotic treatment in a cell divided by a diaphragm impermeable by the particles into anode and cathode compartments, one of which is filled with the suspension and the other with a dielec. liquid such as transformer oil or glycerol. A d. c. of high potential is used and the particles are deposited on the diaphragm (which may be of parchment or powdered Cr oxide).

**Electrodeposition of rubber, yeast, etc.** SIEMENS-ELEKTRO-OSMOSE GES. Brit. 307,830, March 14, 1928. Direct current of high potential (suitably 2000 v.) is used

for depositing substances such as rubber from aq. suspensions to which a dielec. liquid such as glycerol or transformer oil is added. Rubber seps. at the anode but sepn. at the cathode may be effected by adding to the latex a small proportion of a suitable colloid or of a compd. such as Th nitrate. Deposition of yeast in a 3-compartment cell using 50 milliamps. at 10,000 v. is described.

**Former apparatus for deposition of rubber from aqueous dispersions.** W. A. GIBBONS (to Morgan & Wright). Brit. 307,790, March 13, 1928. Structural features of a sectional annular former are described. Brit. 307,791-2 (A. W. Keen to Morgan & Wright) also relate to app. for similar use.

**Mold for electrophoretic deposition of rubber, etc.** E. HAZELL (to Morgan & Wright). Brit. 307,789, March 13, 1928. A perforated metal or other support is covered with a pervious fabric over which may be placed a layer of filtering material such as kieselguhr, clay, infusorial earth or paper pulp, with or without a binder. The mold may be in tubular form.

**Preserving rubber.** J. TEPPEMA (to Goodyear Tire & Rubber Co.). Brit. 308,249, March 20, 1928. Aminoazo hydrocarbons are added to improve the "aging qualities" of rubber.

**Uniting rubber with other materials.** HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,732,886, Oct. 22. The surface of metal, glass, bakelite or other material to which the rubber is to be united is coated with a thin film of a tacky rubber isomer compn., heated to render the film substantially dry; a rubber compn. is then united with the coated surface under pressure.

**Attaching rubber to wood, leather or other materials.** NEDERLANDSCHE GUTTA-PERCHA MAATSCHAPPIJ. Brit. 307,731, March 12, 1928. A suitable adhesive consists of a mixt. of *Hevea* latex and a latex of low rubber and high resin content such as jelutong. Grooves or projections in or on the leather, wood or other material may be utilized to facilitate union with the rubber.

**Uniting layers of fabric, rubber and other materials with adhesives in making waterproof footwear.** ALFRED A. GLIDDEN and WALTER R. HICKLER (to Hood Rubber Co.). U. S. 1,731,740-1, Oct. 15. Various details of manuf. are specified.

**Apparatus for making rubber tubes by extrusion.** C. S. MCCHESENEY and H. H. CLARK (to Dunlop Rubber Co., Ltd.). Brit. 308,209, March 19, 1928. Structural features.

**Rubber tires.** I. G. FARBERIND. A.-G. Fr. 660,634, Sept. 19, 1928. Pneumatic or solid tires are made from products obtained by polymerizing butadiene.

**Thermoplastic product from rubber.** HARRY L. FISHER (to B. F. Goodrich Co.). U. S. 1,731,488, Oct. 15. A non-tacky, readily thermoplastic compn. suitable for molding is obtained by prepg. a vulcanized isomeric conversion product of rubber (suitably by use of *p*-toluenesulfonic acid and S), melting the product and then cooling it.

**Synthetic rubber.** RAY P. DINSMORE (to Goodyear Tire & Rubber Co.). U. S. 1,732,795, Oct. 22. A hydrocarbon such as isoprene is treated with an emulsifying ingredient such as oleic acid and  $\text{NH}_3$  and with casein or other suitable protein, and then heated at 50-70° to effect polymerization.

**Synthetic rubber.** I. G. FARBERIND. A.-G. Brit. 307,808, Sept. 12, 1927. In polymerizing butadiene obtained from  $\text{C}_2\text{H}_2$ , the latter is produced from  $\text{CH}_4$  or from gases contg.  $\text{CH}_4$  in order to obtain  $\text{C}_2\text{H}_2$  free from substances deleterious to the subsequent reactions. An example is given of the passage of a gaseous mixt. contg.  $\text{CH}_4$  through a flaming arc, with details of the conversion of the resulting  $\text{C}_2\text{H}_2$  into butadiene, etc.

**Synthetic rubber.** I. G. FARBERIND. A.-G. Brit. 307,937, March 16, 1928. Preliminary to polymerizing diolefins, such as isoprene or butadiene, the emulsion is homogenized, as by forcing it through narrow openings.

**Synthetic rubber.** I. G. FARBERIND. A.-G. Brit. 307,938, March 17, 1928. Emulsions of diolefins for the production of synthetic rubber are produced by emulsifying together an aq. soln. of an emulsifying agent such as Na oleate and a soln. in a diolefin of the same or a similarly acting emulsifying agent such as a soln. of Mg oleate in butadiene. The emulsions formed may be polymerized with or without homogenization. Several examples are given.

**Rubber-vulcanization accelerators.** DONALD H. POWERS (to E. I. Du Pont de Nemours & Co.). U. S. 1,732,532, Oct. 22. Accelerators are produced by reaction or condensation between 2 mol. proportions of an aldehyde, 2 mol. proportions of an amine (particularly a primary amine), and either 1 or 2 mol. proportions of  $\text{CS}_2$ . Similar products may be obtained by treating an anhydroaldehydeamine with  $\text{CS}_2$  or by treating with an aldehyde the substituted  $\text{NH}_4$  salt of a mono-substituted dithiocarbamic acid. As the aldehydes, there may be used formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde or benzaldehyde; and, among the primary amines which may be

used are methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, hydroxyethylamine, aniline, *o*-toluidine, *p*-toluidine or similar compds. Various examples and details are given.

**Rubber-vulcanization accelerator.** CLAYTON O. NORTH (to Rubber Service Laboratories Co.). U. S. 1,732,770, Oct. 22. Vulcanization with S is accelerated by use of a compd. obtained by the reaction of CS<sub>2</sub> on an aldehyde deriv. of Schiff's base, such as may be prepd. from heptaldehyde and aniline.

**Rubber vulcanization.** I. G. FARBENIND. A.-G. Brit. 308, 275, March 20, 1928. Vulcanization is accelerated by use of a 2-mercaptoarylthiazole substituted in the benzene nucleus by an alkoxy group in the *o*-position to the thiazole N, *e. g.*, 4-methoxy-6-chloro-2-mercaptobenzothiazole.

**Vulcanization of rubber.** THEODORE DÜRST. Fr. 661,190, Jan. 16, 1928. The heated vulcanization gases or air are circulated rapidly in a closed cycle.

**Vulcanizing rubber.** WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,732,486, Oct. 22. Rubber and S are heated together in the presence of a mixt. of accelerators comprising the reaction product of dinitrochlorobenzene and an alk. salt of mercaptobenzothiazole and a basic org. N-contg. accelerator such as diphenylguanidine. Many examples are given.

**Vulcanized rubber.** THOMAS W. MILLER (to Faultless Rubber Co.). U. S. 1,732,944, Oct. 22. A vulcanized rubber of good tensile strength and aging properties is obtained by the use of vulcanizing of 2 different accelerators such as tetramethylthiurammonosulfide and ethylidene-aniline or (CH<sub>3</sub>)<sub>2</sub>N<sub>2</sub>, either of which in the presence of an activating agent such as ZnO is effective at a relatively low temp. and the second of which is operative at temps. of about 120°. Certain of the ingredients for vulcanization are incorporated in the rubber batch and others (such as the tetramethylthiurammonosulfide) are incorporated in a hot water bath in which the vulcanization is effected. The vulcanization is thus rapidly effected at a relatively low temp.

**Vulcanized rubber compositions.** LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,732,774, Oct. 22. A product formed by the interaction of a crotonaldehyde and an amine such as aniline, toluidines, xylidines or naphthylamines in the presence of an acidic substance such as HCl is used for preserving the compns. against atm. deterioration.

**Vulcanizing mold for inner tubes of rubber tires.** P. DE MATTIA (to National Rubber Machinery Co.). Brit. 308,364, March 22, 1928. Structural features.

**Apparatus for vulcanizing rubber tires.** R. W. BROWN (to Firestone Tire & Rubber Co. (1922), Ltd.). Brit. 307,897-8, March 16, 1928. Structural features.

**Rubber latex.** AKTIEBOLAGET SEPARATOR. Fr. 662,528, Oct. 19, 1928. The latex contained in the deposit formed in tanks for storing rubber latex is recovered by centrifuging.

**Coagulating latex.** I. G. FARBENIND. A.-G. Brit. 309,245, Jan. 23, 1928. Coagulation of latex is effected by addn. of an acid such as HOAc or HCl in the presence of an org. substance such as aromatic or hydroaromatic sulfonic acids which contain alkyl, cycloalkyl, aralkyl, or aryl groups in the nucleus or in other substituents such as amino or hydroxyl groups, true sulfonic acids of aliphatic tar, or of mineral oils, fatty acids, naphthenic acids and the like, fat-splitting substances, sulfonic acids having tannin properties, or salts of these sulfonic acids. Examples are given.

**Rubber.** THE ANODE RUBBER Co. (England), LTD. Fr. 661,497, Oct. 4, 1928. A transparent vulcanized rubber is obtained by adding S and an ultra-accelerator such as Zn diethyldithiocarbamate, Zn piperidinecarbothionolate or Zn alkylxanthate to a natural latex and vulcanizing. The latex may be freed by dialysis of part of the serum before addn. of the other substances.

**Rubber.** THE ANODE RUBBER Co. (England), LTD. Fr. 661,792, Oct. 5, 1928. Objects having at least a pasty consistency, non-coagulated or partly coagulated, produced from aq. dispersions of substances of the nature of rubber, are put in the nascent and damp state into contact with a liquid sol. in or miscible with water which will eliminate a part of the water and at the same time have a coagulating action. The water-eliminating liquid may be composed of an aq. soln. of NH<sub>4</sub> and an org. acid such as AcOH, or a fused cryst. salt melting at a temp. below 100°.

**Rubber.** IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 661,480, Oct. 4, 1928. In the elec. deposition of rubber or the like from an aq. dispersion the dispersion is modified by the addn. of an org. compd. which forms on oxidation at the anode a vulcanization accelerator which becomes incorporated in the deposit. Suitable compds. are Na diethyldithiocarbamate, hydroquinol and a dimercaptan.

**Pigments for coloring rubber.** IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 661,481, Oct. 4, 1928. Rubber, gutta-percha and like resins are colored by incorporating in the mix a pigment consisting of a vat dye and a finely divided substratum substantially



insol. in water. Suitable substrata are barytes,  $\text{Al}_2\text{O}_3$ , whiting, clays,  $\text{SiO}_2$ , talc, asbestos, lithopone, Zn white, etc., which may be mixed with a dispersed paste or suspension of the dye. Examples are given.

**Preserving rubber.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 309,161, April 7, 1928. Reaction products of S and an amine, e. g., thiophenylamine, thiophenyl- $\beta$ -naphthylamine, thio- $\beta$ -dinaphthylamine or phenyl- $\alpha$ -naphthylamine (the prepn. of which is described) are used as "anti-agers." Cf. C. A. 24, 265.

**Reinforced sheet rubber.** BRUCE W. ROGERS (to B. F. Goodrich Co.). U. S. 1,733,469, Oct. 29. Layers are united by vulcanization which include a facing layer of abrasion-resisting, soft-rubber compd. and a flexible fabric backing which comprises a layer of woven fabric next to the facing layer and a layer of relatively stiff, semi-hard rubber compd. next to the fabric layer. Sheet material thus formed is suitable for lining chutes, etc.

**Rubber products.** DUNLOP RUBBER CO., LTD., W. H. CHAPMAN and F. H. LANE. Brit. 308,626, Sept. 24, 1927. Deposits obtained by dipping, molding, spraying, electrophoresis or otherwise are dried by pressing them between or against porous or other surfaces through which water can escape such as cloth, blotting paper or ceramic materials. Various mech. details are described.

**Rubber filaments.** M. DRAEMANN. Brit. 308,706, March 27, 1928. Rubber filaments are given a protective coating of rubber which may be colored by passing through a bath of rubber soln. which may contain S, Zn white, chalk or other coloring matter and may then be coated with powdered talc or vulcanized if desired. An app. is described.

**Attaching rubber to other surfaces.** W. B. WESCOTT (to Rubber Latex Research Corp.). Brit. 309,168, April 6, 1928. A film of protein material treated to render it resistant to water is used for attaching rubber or the like to metals, synthetic resins, wood, etc., for lining vats, cementing tires to wheels, etc. Various details are given.

**Method of uniting crepe rubber to leather, etc., and plant therefor.** ERNST ENNA. Ger. 483,245, Mar. 27, 1925.

**Utilizing waste rubber.** L. B. CONANT. Brit. 309,319, April 21, 1928. Old solid rubber tires are sliced and die-cut to form shoe soles. Excess of S may be removed from the rubber with a caustic soln.

**Recovering rubber.** SYNDICAT FRANCO-NÉERLANDAIS. Ger. 483,093, June 5, 1927. Addn. to 460,563. See Brit. 276,626 (C. A. 22, 2494).

**Synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 308,755, March 31, 1928. Special proportions of materials and reacting conditions are described for operation of the process described in Brit. 283,841 (C. A. 22, 4274). Various details and examples are given. Cf. C. A. 24, 266.

**Plastic compositions.** JEAN BAER. Swiss 132,509 to 132,515, Oct. 20, 1926. Addns. to 127,540. An elastic rubber-like mass is produced by the action of methylene or ethylene dihalide on S or polysulfide in the presence of a solvent, with or without addn. of  $\text{CH}_2\text{O}$ . Filling material such as ZnO, soot, MgO or natural rubber may be added. Cf. C. A. 23, 5062.

**Aqueous dispersions of factice and other rubber substitutes.** K. D. P., LTD. Brit. 309,167, April 7, 1928. The substances are treated with a dispersing agent such as gelatin, casein, soaps, saponin or alkalies, in a roller mill, and water (with or without addnl. dispersing agent) is added during the process.

**Tire-tube vulcanizing apparatus.** E. FETTER. Brit. 309,311, April 13, 1928. Structural features.

**"Age-resisting" vulcanized rubber.** MAX H. ZIMMERMANN (to Albert C. Burrage, Jr.). U. S. 1,734,951, Nov. 5. Vulcanization is effected in the presence of diphenylnitrosoamine. U. S. 1,734,952 specifies the use of di- $\alpha$ -naphthylnitrosoamine. U. S. 1,734,953 specifies the use of phenyl- $\alpha$ -tolynitrosoamine or other suitable diaryl substituted nitrosoamine contg. a methyl substituent in the aryl nucleus.

**Vulcanizing rubber.** HENRY B. MORSE (to Albert C. Burrage, Jr.). U. S. 1,734,633, Nov. 5. Di- $\beta$ -naphthylnitrosoamine is used to control accelerators and inhibit their premature action. U. S. 1,734,634 specifies the use of an org. "ultra-accelerator" such as mercaptobenzothiazole together with diphenylnitrosoamine or other suitable disubstituted nitrosoamine contg. hydrocarbon radicals as substituents, which serve to control the accelerator. U. S. 1,734,635 relates to the control of the action of an org. accelerator such as mercaptobenzothiazole by the use of a dinaphthylnitrosoamine. U. S. 1,734,636 relates to the use of phenyl- $\alpha$ -naphthylnitrosoamine or other unlike substituted nitrosoamine contg. an aryl and a naphthyl radical substituent. U. S. 1,734,637 relates to the use of phenyl- $\beta$ -naphthylnitrosoamine or other suitable aryl- $\beta$ -naphthylnitrosoamine. U. S. 1,734,638 relates to the use of phenyl- $\alpha$ -tolynitrosoamine or other suitable diaryl substituted nitrosoamine contg. a methyl radical in one of the aryl nuclei.

U. S. 1,734,639 specifies the use of phenyl-*p*-tolynitrosoamine or other aryl *p*-tolynitrosoamine. U. S. 1,734,640 relates to the use of di-*o*-tolynitrosoamine or other diaryl substituted nitrosoamine, both aryl radicals of which contain a methyl group.

**Rubber compositions.** JAMES H. REEL and HAROLD E. CUDE (to Naugatuck Chemical Co.). U. S. 1,735,547, Nov. 12. Phase-reversible compns. are prep'd. by agitating water, oil, rubber and a water-insol. soap as emulsifying agent until a uniform dispersion is obtained, converting the insol. soap into sol. form with an alkali, and then agitating to effect a reversal of phase.

**Electrodeposition of rubber.** SIEMENS & HALSKE A.-G. Brit. 309,947, April 18, 1928. Rubber deposited from latex on an electrode or on a porous mold in front of the electrode by a. c. as described in Brit. 307,747 (C. A. 24, 265) is immersed immediately after leaving the electrolytic bath, and while still on its support, in an acid soln. such as HOAc, weak HCl or CO<sub>2</sub>.

**Deposition of rubber.** THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 663,114, Oct. 27, 1928. Moisture contained in coatings obtained from aq. dispersions of rubber or the like is eliminated by obtaining the layer of rubber on a conducting support, covering the outer surface of the layer with a conducting material and passing a current through the layer.

**Porous molds for rubber deposition.** NAUGATUCK CHEMICAL CO. Brit. 310,302, Jan. 21, 1928. Hollow forms such as those of perforated Al are covered with a layer of filtering material which may be formed of paper pulp and whiting or of material such as diatomaceous earth with various binders such as clay and magnesia or a rubber or synthetic resin compn. A smooth outer layer of clay slip or the like may be applied.

**Molded articles of rubber and fiber.** WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,737,133, Nov. 26. In forming resilient wheels or other molded articles, a mass of fibers in the form of cords 0.5-1.5 in. in length is satd. with rubber latex contg. a coagulable protein such as hemoglobin as a protective colloid, the wet mass is shaped, dried, compressed and cured.

**Zirconium-coated mold for curing tires or other rubber articles.** ANTON BOERDER. U. S. 1,735,916, Nov. 19.

**Rubber articles.** C. MACINTOSH & CO., LTD., S. A. BRAZIER and G. F. THOMPSON. Brit. 310,602, Feb. 22, 1928. Articles with an ebonite exterior such as ball floats, croquet balls, etc., are formed from an uncured ebonite sheet by shaping on a rubber former (which then becomes a part of the article) and vulcanizing. The former may be of sponge rubber, or may be inflatable.

**Rubber articles from dispersions.** P. KLEIN and ANODE RUBBER CO. (England), LTD. Brit. 309,630, Jan. 14, 1928. Articles are made directly from 2 or more aq. dispersions contg. different proportions of masticated rubber, gutta, balata or the like, by dipping, electrophoresis, spreading, spraying, impregnating or extruding. A coating dispersion may be added to the bath in which the article is formed.

**Porous rubber.** H. BECKMANN (to K. D. P., Ltd.). Brit. 309,575, April 14, 1928. Albuminous or albumin-decompn. products, e. g., casein, are added to latex in prep'g. microporous rubber as described in Brit. 240,430 (C. A. 20, 2262) to delay setting and facilitate subsequent shaping.

**Uniting different materials by use of rubber.** L. B. SEBRELL (to Goodyear Tire & Rubber Co.). Brit. 310,461, April 26, 1928. Fibrous or porous materials are secured to metals or to each other by joining and heating them together after treatment with a rubber cement preliminarily treated with a polymerizing agent such as SnCl<sub>4</sub> or other halide salt of an amphoteric metal. Various details are given.

**Insulating electric conductors.** CHARLES R. BOGGS (to Simplex Wire & Cable Co.). U. S. 1,736,899, Nov. 26. A cond. core is covered with synthetic rubber substantially free from active rubber-dispersing agents or non-rubber constituents acting as protective colloids for the rubber and adapted to resist water.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Fr. 663,995, Nov. 15, 1928. Emulsions similar to latex and masses of a rubber-like nature are obtained by polymerizing 1,3-butadiene or its homologs in the presence of aq. solns. of salts of biliary acids or their derivs. or in the presence of animal bile. Examples are given using Na cholate, Na desoxycholate and ox bile.

**Use of isopropyl monoxanthogen as a rubber vulcanization accelerator.** GEORGE S. WHITBY (to Roessler & Hasslacher Chemical Co.). U. S. 1,735,701, Nov. 12.

**Use of rubber solution containing a vulcanizer for waterproofing blasting fuses.** W. ESCHBACH and F. HABBEL. Brit. 310,364, April 24, 1928. The rubber coating is vulcanized by a hot or cold process.

**Aldehyde-amine reaction products (rubber vulcanization accelerators).** CLAYTON O. NORTH and WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,737,384, Nov. 26. Heptaldehyde is caused to react with butyldenedianilide (formed by reaction

of butyric aldehyde with 2 mol. proportions of aniline). Various other similar starting materials may also be caused to react similarly to form vulcanization accelerators.

**Aldehyde-amine reaction products (rubber vulcanization accelerators).** WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,737,391, Nov. 26. Two mol. proportions of a secondary amine such as dibenzylamine are caused to react with an aldehyde such as paraformaldehyde, and the product thus formed (suitably while dissolved in ether) is caused to react with  $\text{CS}_2$ .

**Vulcanization of rubber.** I. G. FARBERNIND. A.-G. Fr. 663,255, Oct. 31, 1928. Vulcanization of rubber is carried out in the presence of alicyclic bases of the formula

$\begin{matrix} R^1 \\ \diagup \\ N-X, \end{matrix}$  in which  $R^1$  represents an alicyclic group combined with N either directly or indirectly through one or more C atoms,  $R^2$  represents a univalent org. radical, such as an alicyclic group combined directly or indirectly, an alkyl, aryl or aralkyl radical, which may be combined with  $R^1$  to form a ring, and X represents H alone or in combination

with an aldehyde or an acid, the group  $\begin{matrix} -C-S \\ || \\ S \end{matrix}$  or again the group  $\begin{matrix} -C-N \\ || \\ Y \end{matrix} \begin{matrix} R \\ \diagup \\ R \end{matrix}$ , in which R may be H or one of the groups indicated by  $R^1$  or  $R^2$ , and Y designates S, O or N-R. Examples are given.

**Rubber.** AKTIEBOLAGET SEPARATOR. Fr. 664,183, Nov. 20, 1928. Impurities in suspension in latex are eliminated by centrifuging before pptn. of the rubber by known means. If a preserving substance such as  $\text{NH}_3$  is added, it is advantageous to centrifuge after such addn. Cf. C. A. 24, 527.

**Rubber.** FRITZ KEMPTER. Fr. 664,823, Nov. 29, 1928. Solns. of rubber are prepd. in known mixing app. of the Werner and Pfeleiderer type, in which the walls which are swept by the agitators have friction surfaces.

**Rubber from plants.** THOMAS A. EDISON (to Edison Botanic Research Corp.). U. S. 1,740,079, Dec. 17. Bark and pithy material of plants such as guayule are sepd. from the woody material without disintegrating the latter, and the bark and pithy material only are treated for extrn. of rubber, e. g., by pulping and gravity sepn.

**Thickening latex.** S. D. SUTTON and VEEDIP, LTD. Brit. 312,947, Jan. 2, 1928. A small proportion of  $\text{ZnO}$  is added, suitably after excess  $\text{NH}_3$  and serum constituents have been removed by flowing over hot plates or adding boric acid or  $\text{HOAc}$ .

**Apparatus for forming tubing from solutions or aqueous dispersions of rubber, gutta-percha, balata, etc.** DOUGLAS F. TWISS and EDWARD A. MURPHY (to Dunlop Rubber Co., Ltd.). U. S. 1,738,268, Dec. 3. Structural features.

**Artificial gutta-percha.** EDUARD S. ALI-COHEN. U. S. 1,739,566, Dec. 17; Brit. 313,373, Sept. 5, 1928. Dild. latex is added to a hot homogeneous emulsion of resins and waxes such as colophony, shellac and beeswax in an alkali soap soln., and coagulation is effected with a sol. Al salt such as alum.

**Rubber compositions.** I. G. FARBERNIND. A.-G. Brit. 311,372, May 10, 1928. In forming vulcanizing compns., Se or Se compds. are incorporated in a colloidal state into natural or artificial rubber. Various details of procedure are given.

**Rubber compositions.** DUNLOP RUBBER CO., LTD., W. H. CHAPMAN and P. D. PATTERSON. Brit. 313,027, March 5, 1928. Compounding ingredients such as  $\text{ZnO}$ , lampblack, non-colloidal clays, fibrous materials, oils, S and mercaptobenzothiazole, which are to be incorporated in rubber latex or the like, are first intimately mixed with a material which is already plastic and dispersible in an aq. medium, e. g., colloidal clay or colophony, or which can be rendered plastic, e. g., rubber, rubber waste or reclaim, synthetic rubber or thermoplastic rubber compns., and the mixt. is then dispersed and the dispersion is added to the latex. Various details and examples are given. Brit. 313,028 relates to the similar preliminary admixt. and dispersion of gas black which is to be incorporated as a filler with rubber latex.

**Rubber compositions.** S. A. J. HOLMQUIST. Brit. 313,369, Aug. 24, 1928. Disintegrated fibrous material such as linen and hemp, 30-70 parts is mixed with 70-30 parts shredded vulcanized rubber products which may contain fabric, by grinding to fine subdivision. The mixt. is then incorporated with 25-75% unvulcanized rubber, and fillers, coloring substances, etc., may be added and the product may be formed into shoe soles, sheets or other articles.

**Retarding aging or rubber compositions.** ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,739,480, Dec. 10. A reaction product of a naphthylamine and an aliphatic acid such as  $\alpha$ -formylnaphthylamine or similar compds. is used in the manuf. of vulcanized rubber products. Cf. C. A. 23, 5353.

**Rubber dispersions.** METALLGES. A.-G. (to K. D. P., Ltd.). Brit. 311,268, May

8, 1928. For regenerating vulcanized rubber and dispersing it in water, it is treated in a roller mill or like app. with a dispersing agent such as glue, soap, casein, gelatin or saponin, and about 30% of water is subsequently added. Vulcanizing agents and latex, also may be added to produce a compn. suitable for waterproofing fabrics.

**Deodorizing rubber.** DUNLOP RUBBER CO., LTD., and E. W. MADGE. Brit. 312,443, March 29, 1928. Electrophoretically deposited rubber is deodorized, before or after vulcanization, by treatment with  $\text{CH}_2\text{O}$  or an aq. soln. of paraformaldehyde, and the odor of  $\text{CH}_2\text{O}$  may then be removed by treatment with  $\text{NH}_3$ . Addn. of  $\text{Na}_2\text{CO}_3$  accelerates the action of the  $\text{CH}_2\text{O}$ .

**An electric heating apparatus for heating the cores used in the manuf. of rubber articles from latex.** SOCIETÀ ITALIANA PIRELLI. Fr. 664,844, Nov. 29, 1928.

**Molds for rubber.** ALFRED VOSHAGE. Fr. 665,073, Dec. 4, 1928. Molds for the vulcanization of rubber are sprayed with a soln. of an alkali silicate, then a 2nd thin layer formed by a soln. of a substance of the nature of sugar is applied, to give brilliant vulcanized articles not sticking to the mold.

**Coating rubber dentures or other articles with metals.** H. PAWECK (to M. Ow-Eschingen). Brit. 311,766, May 16, 1928. Coating with Au, Ag or other metal is effected by treating the articles in a soln. of a reducing agent in a solvent which will cause the rubber to swell, drying to leave the reducing agent distributed on and in the surface layers, then passing the article through a bath of a reducible metal salt, drying and repeating these steps until a sufficient deposition of metal is effected. Various details and examples are given.

**Rubber coatings on metals.** ALEXANDER JENNY. Fr. 665,571, Dec. 12, 1928. See Brit. 302,250 (C. A. 23, 4375).

**Treating embossed leather or other materials with rubber, etc.** C. MACINTOSH & CO., LTD., S. A. BRAZIER and A. B. HATTON. Brit. 311,982, July 13, 1928. After embossing, the material is treated with an aq. dispersion of natural or artificial rubber, so that the depressions in the material are filled and a two-color effect is produced.

**Use of porous rubber powder or granules as a filtering medium or absorbent for liquids or gases, or for lubricating pads.** H. BECKMANN. Brit. 313,052, June 5, 1928. The rubber used may be prepd. as described in Brit. 240,430 (C. A. 20, 2262).

**Increasing the resistance to wear of rubber.** J. J. M. KLUIJTMANS. Belg. 358,256, March 31, 1929. An abrasive such as silicate, sand, emery or carborundum is incorporated with the rubber.

**Preserving rubber.** DUNLOP RUBBER CO., LTD., A. E. T. NEALE and F. THOMAS. Brit. 311,930, May 5, 1928. The rubber has added to it about 1% of the condensation product of *p*-aminophenol and acetaldoal or a similar condensation product.

**Preserving rubber.** W. L. SEMON (to B. F. Goodrich Co.). Brit. 312,630, May 29, 1928. The "ageing" qualities of rubber are improved by the addn. of disubstituted *p*-phenylenediamines. Numerous examples are given.

**Forming threads, tubes, etc., from rubber.** DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 311,844, Feb. 23, 1928. An aq. dispersion such as a latex compn. is caused to flow through jets of the desired shape into a bath contg. a dehydrating and setting medium such as is described in Brit. 290,313 (C. A. 23, 1012). An app. and various details of procedure are described.

**Extrusion apparatus for manufacture of rubber articles.** GEORGE E. FOERSTNER (to B. F. Goodrich Co.). U. S. 1,740,082, Dec. 17. Structural features.

**Apparatus for manufacture of rubber inner tubes, etc., by extrusion.** CHARLES S. MOOMY. U. S. 1,740,029, Dec. 17. Structural features.

**Reclaiming rubber from scrap.** LEE T. SMITH (to Hercules Powder Co.). U. S. 1,737,775, Dec. 3. Scrap contg. rubber and fabric is treated with dipolymer to dissolve the rubber, and the rubber is recovered from the resulting soln. by pptn. with an acetone.

**Rubber synthesis.** I. G. FARBENIND. A.-G. Brit. 311,381, May 10, 1928. In production of synthetic rubber by a process in which an artificial latex is produced and coagulation is effected by cooling below  $0^\circ$ , as described in Brit. 304,207 (C. A. 23, 4848), sepn. of the emulsifying agent used is facilitated by removing the unchanged diolefin before or after the cooling but before the washing of the coagulum. Such removal may be effected by evapn. by various alternative methods which are described.

**Artificial rubber.** I. G. FARBENIND. A.-G. Fr. 664,419, Nov. 22, 1928. Artificial rubber is prepd. by polymerizing butadiene hydrocarbons in the presence of latex or substances resembling latex and vulcanizing. Cf. C. A. 23, 4102, 4103.

**Artificial rubber.** I. G. FARBENIND. A.-G. Fr. 665,537, Dec. 11, 1928. Products resembling rubber are obtained by mixing polymers of 1,3-butadiene or of a homologous or analogous hydrocarbon which have been obtained under different conditions, mixts. of polymers of 2,3-dimethyl-1,3-butadiene being excepted, and vulcanizing. Cf. preceding abstr.



**Rubber substitute.** E. KLEIBER and P. GILARDI. Brit. 312,741, March 26, 1928. Petroleum is treated with  $\text{HNO}_3$  or with  $\text{Na}_2\text{O}_2$  in the presence of soda lime or  $\text{NaOAc}$ , or with other suitable oxidizing agent, and the neutralized liquid which is thus obtained is distd. repeatedly over colophony; the distillate is heated under pressure with dil. alkali and seps. into 3 layers. One or both of the upper layers are treated with a "rubber promoter" such as glacial  $\text{HOAc}$  and  $\text{CH}_3\text{O}$  and raw rubber, and by the addn. of acetone or alc. to the sirup-like mass, an elastic mass is produced which can be vulcanized. The residue from the distn. over colophony may be used as a copal substitute in making varnish.

**Polymerized diolefins.** I. G. FARBERNIND. A.-G. Brit. 313,188, Feb. 9, 1928. Polymerization is effected in the presence of latex or similar vegetable saps and of oxidizing or emulsifying agents (of which numerous examples are given). The product may be vulcanized and synthetic resins may be added to it.

**Vulcanized oils.** IMPERIAL CHEMICAL INDUSTRIES, LTD., and W. J. S. NAUNTON. Brit. 313,252, April 5, 1928. Linseed oil or other suitable fats or fatty oils contg. a substantial proportion of unsatd. oils are vulcanized at temps. above  $100^\circ$  (suitably in an autoclave at  $160\text{--}70^\circ$ ) when emulsified in a non-solvent liquid such as an aq. mixt. of casein,  $\text{NH}_3$  and  $\text{NH}_4$  oleate, by the action of S, and may be mixed with accelerators, activators, etc.

**Apparatus for vulcanizing rubber.** BENJAMIN GRIFFITH. Fr. 665,154, Dec. 6, 1928.

**Apparatus for vulcanizing rubber articles continuously as they pass through an elongated chamber.** C. DRESSLER and GIBBONS BROS., LTD. Brit. 311,507, March 21, 1928. Various details of construction and operation are described.

**Apparatus for vulcanizing articles such as dental plates.** WM. M. POST. U. S. 1,740,034, Dec. 17. Structural features.

**Apparatus for vulcanizing inner tire tubes, etc.** HENRY C. BOSTWICK (to Akron Standard Mold Co.). U. S. 1,740,065, Dec. 17. Structural features.

**Accelerators for rubber vulcanization.** LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,739,486, Dec. 10. In making triphenylguanidine or other substituted guanidines, basic Pb carbonate and  $\text{PbO}$  are admixed with a thiourea such as thiocarbamilide and a primary amine such as aniline is added, and the materials are heated (suitably to a temp. of about  $100^\circ$ ).

**Rubber vulcanization accelerators.** I. G. FARBERNIND. A.-G. Brit. 311,735, May 15, 1928. *p*- or *o*-Tolylaminoimidazoline or a non-substituted aryl deriv., or similar compds. are used as accelerators.

**Rubber vulcanization accelerators.** I. G. FARBERNIND. A.-G. Brit. 312,069, May 18, 1928. Liquid derivs. of guanidine such as pentamethylguanidine and pentabutylguanidine are used as accelerators in vulcanizing natural or synthetic rubber.

**Treating rubber latex.** JOHN MCGAVACK (to General Rubber Co.). U. S. 1,740,994, Dec. 24. See Brit. 294,002 (C. A. 23, 1777).

**Rubber.** THE ANODE RUBBER CO., LTD. Ger. 485,528, May 19, 1926. A process for the direct production of rubber ware from the milk is described.

**Electrical apparatus for producing rubber articles.** THE ANODE RUBBER CO., LTD. Ger. 484,864, July 31, 1924. An elec. app. is described for producing plates and other shaped ware directly from aq. dispersions of rubber and rubber-like substances.

**Deposition of rubber, etc.** THE ANODE RUBBER CO. (England), LTD. Fr. 667,083, Jan. 8, 1929. A process for the manuf. of fabric articles proofed or impregnated with org. materials such as rubber, and of sheets of such org. materials, is described.

**Rubber composition.** PAUL C. JONES (to B. F. Goodrich Co.). U. S. 1,741,778, Dec. 31. Tetraphenylhydrazine is incorporated in rubber before vulcanization to serve as a preserving agent.

**Rubber compositions.** JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,742,609, Jan. 7. In order to increase the flexing value of vulcanized rubber compns., they are treated before vulcanizing with compds. such as thymoquinone, nitrosothymol,  $\alpha$ -naphthoquinone or  $\beta$ -naphthoquinone.

**Rubber compositions.** I. G. FARBERNIND. A.-G. Brit. 313,919, June 19, 1928. Natural or artificial rubber (preferably in a solvent such as  $\text{CCl}_4$ ) is treated with an alkyl or aryl S halide or deriv. such as *p*-nitrophenyl chloride. A bright yellow powder sintering at  $135^\circ$  may be obtained. Cf. C. A. 24, 988.

**Coloring rubber.** ELMER G. CROAKMAN (to National Aniline & Chemical Co.). U. S. 1,742,757, Jan. 7. A triarylmethane dye base such as "Victoria blue B base" and an aromatic nitro compd. such as 2,4-dinitrophenol are incorporated with a rubber mixt. and the latter is vulcanized by heat.

**"Antiaagers" for use in rubber compositions.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 313,486, June 12, 1928. Compds. are used such as 2-hydroxy-



1,4-anilidonaphthoquinone, 1,4-anilidonaphthoquinoneaniline and 1,4-anilidonaphthoquinoneaniline.

**Factice and similar compositions.** J. BAER. Brit. 313,917, June 19, 1928. Oil such as rapeseed oil is heated with the polymerization product obtained by treating satd. halogenized hydrocarbons such as ethylene dichloride with S or S-yielding substances such as Ca polysulfide, to produce a factice sol. in  $C_6H_6$ ,  $CHCl_3$ , ethylene chloride and like solvents.

**Lampblack.** I. G. FARBENIND. A.-G. Fr. 667,786, Jan. 19, 1929. Lampblack for use in the rubber industry or for ink is made by passing heated CO under pressure over mixts. of metals of the 8th group of the periodic system among themselves or with their compds. or with other compds.

**Rubber fabric.** JEROME MAYER (to Comfolastic Corp.). U. S. 1,741,530, Dec. 31. A fabric such as knitted rayon is moistened, stretched in one direction and allowed to set in the stretched condition; a sheet of rubber is then vulcanized onto one face of the fabric to give it elasticity in a direction transverse to the direction of initial stretching.

**Waterproofing composition containing rubber.** ALLEN F. OWEN (to Naugatuck Chemical Co.). U. S. reissue 17,541, Dec. 31. See original U. S. 1,656,953 (C. A. 22, 1019) and Can. 266,291 (C. A. 21, 996).

**Apparatus for testing the compressibility and thus grading rubber balls, etc.** DUNLOP RUBBER CO., LTD., and T. CROPPER. Brit. 313,683, April 4, 1928. Structural features.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 312,949, Jan. 2, 1928. Diolefins are emulsified with an aq. soln. or emulsion which may comprise milk, glue, gelatin and other albuminous substances and the mixt. is allowed to stand until 2 layers are formed, one of which is a creamy or gelatinous mass contg. at least 75% of diolefin and in which the aq. component is in the disperse phase; the gelatinous mass is then polymerized, suitably with use of agents such as O,  $H_2O_2$ , benzoyl peroxide,  $NH_4$  persulfate or  $BaO_2$ . Various details and examples are given.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 312,201, Dec. 19, 1927. Diolefins such as butadiene and its homologs are emulsified, dispersed or dissolved in aq. media by use of soap-like dispersing agents such as sulfonic acids or their salts, or oleates, and then polymerized, suitably in the presence of buffer solns. of fixed  $pH$  such as 4 to 8.5, to produce products similar to latex. Polymerization may be facilitated by use of substances such as  $H_2O_2$ , urea- $H_2O_2$  or other peroxides or ozonides. Numerous details of prepn. and coagulation of the artificial latex, etc., are described.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Fr. 667,256, Jan. 11, 1929. Aq. emulsions of polymerization products of butadiene-(1,3) or of its homologs or analogs are coagulated by cooling the emulsions to a temp., e. g.,  $-14^\circ$  to  $-20^\circ$  which causes them completely to congeal.

**Fuel for use in vulcanizing rubber.** PAUL F. M. A. FONTANA. Fr. 667,711, April 21, 1928. A suitable fuel is obtained by solidifying  $CH_2O$  or para- $CH_2O$  with a soln. of resin in alc.

**Rubber.** THE ANODE RUBBER CO. Ger. 485,797, Sept. 5, 1925. A homogeneous rubber ppt. is prepd. by elec. pptn. from an aq. dispersion contg. also a metallic ppt. Cf. C. A. 24, 1249.

**Rubber.** IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 666,045, Dec. 19, 1928. The dispersion of ingredients for rubber manuf. is facilitated by coating the particles with a dispersing agent such as oils, fatty acids, waxes and rubber softeners in general. The dispersing agent may be dissolved or dispersed in a liquid in which the ingredient is insol., and the dispersing agent may combine with the ingredient.

**Centrifugalization of rubber latex.** O. E. FRÖDING (to Aktiebolaget Separator). Swed. 67,471, June 4, 1929. A device is specified for preventing the evapn. or atm. oxidation of the coagulation-preventing substance before the centrifugalization of rubber latex, balata, etc., with an addn. of  $NH_3$ .

**Rubber-latex cement.** BRADLEY DEWEY and ERNEST C. CROCKER (Crocker to Dewey). U. S. 1,745,084, Jan. 28. Rubber latex is prepd. with finely dispersed S and a smaller proportion of dispersed bentonite, forming a liquid vulcanizable compn. suitable for use in brush manuf., etc.

**Rubber composition.** ARTHUR B. COWDERY (to Barrett Co.). U. S. 1,743,433, Jan. 14. Rubber stock is mixed with a coal-tar distn. residue contg. about 60% of uncombined C.

**Buoyant and oil-proof rubber composition.** EIZO YOSHIOKA. U. S. 1,744,602, Jan. 21. A compn. which is suitable for making oil hose (which floats on water) is formed from raw rubber 88, factice 3, S 5, alk. soap 3 and diphenylguanidine 1%.

**Coloring rubber.** IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 666,126, Dec. 20, 1928. Rubber or the like, crude or vulcanized, as latex or a suspension or colloid is

colored by incorporating in the suspension a dispersed coloring material which is insol. in water with or without protective colloids.

**Rubber coatings.** FRITZ AHRENS and HARZER ACHSENWERKE G. M. B. H. BORNUM A. HARZ. Fr. 666,143, Dec. 20, 1928. See Brit. 302,935 (C. A. 23, 4375).

**Sponge rubber.** Y. CORNIC. Brit. 314,539, June 29, 1928. Powd.  $(\text{NH}_4)_2\text{CO}_3$  is added to concd. latex contg. an org. base such as diphenylguanidine and soon produces complete coagulation; the molded product is converted into a sponge by heating to  $140^\circ$  in an inert gas, superheated steam or a non-solvent liquid such as glycerol. The initial mixt. may contain S or sulfides, ZnO and fillers, and after the formation of the sponge the crust is removed from it, it is washed with alkali, and may be colored, perfumed and sterilized.

**Molded rubber goods.** A. T. GUSTAFSON. Swed. 64,539, Feb. 7, 1928. A thin foliage of a physically homogeneous, not fibrous org. substance is used as an intermediate layer between the mold and the mass to be molded.

**Rubber sheets.** P. SCHIDROWITZ and D. J. BURKE. Brit. 314,783, April 2, 1928. Thin rubber sheets "for use as artificial leather" are made from a mixt. comprising a finely divided reinforcing agent such as gas black, colloidal clay or light  $\text{MgCO}_3$  in the proportion of 0.5–1.0 vol. for each vol. of rubber, and a rape-seed oil or other fat in the proportion of 0.3–0.7 vol. for each vol. of "reinforcing agent." Softeners such as "mineral rubber," and other substances such as S, accelerators, ZnO, PbO, etc., also may be added. Details of vulcanization, etc., are given.

**Diaphragms.** I. G. FARBERIND. A.-G. Fr. 668,045, Jan. 26, 1929. Products of the polymerization of butadiene which do not distil without decompn. are used for making diaphragms for electrolytic vats, etc.

**Manufacture of rubber tubes and like articles by extrusion.** DUNLOP RUBBER CO., LTD., J. HALL and G. F. McCOMBE. Brit. 314,600, April 4, 1928. An app. and various mech. features of operation are described.

**Making tire tread slabs from blocks of alternate sheets of rubber and fabric material.** VIRGIL C. ANDERSON. U. S. 1,744,025, Jan. 21. Mech. features.

**Dispersed rubber isomer.** HARLAN L. TRUMBULL (to B. F. Goodrich Co.). U. S. 1,744,844, Jan. 28. A rubber isomer is dispersed in an aq. medium contg. a hydrophilic colloid such as casein, glue or bentonite. The products may be used as coating or impregnating compns.

**Adhesive.** WM. C. GEER (to B. F. Goodrich Co.). U. S. 1,744,880, Jan. 28. An adhesive suitable for various purposes comprises tough, balata-like and hard, friable, artificial isomers of rubber which may be formed by heating rubber with *p*-phenolsulfonic acid.

**Synthetic rubber.** GOSUDARSTVENNYI TREST REZINOVOI PROMYSHLENNOSTI (RESINOTREST) and B. W. BYSOW. Brit. 314,932, April 5, 1928. In polymerizing butadiene or its homologs, dimers of diolefins or terpenes are added to the mixt. so that by influencing the equil. of the reaction the undesired production of dimer in the polymerization will be prevented. Dimers of butadiene, dipentene, limonene and ordinary Russian oil of turpentine may be used. Brit. 314,933 specifies effecting similar polymerizations in the presence of substances having tautomeric properties, such as a mixt. of benzoylacetate ester and diazoaminobenzene or a mixt. of benzoylacetate ester and phenyl mustard oil.

**Rubber-like products.** J. BAER. Brit. 314,524, June 29, 1928. Halogen compds. of unsatd. hydrocarbons such as isoprene dibromide or butadiene dichloride are reacted on (suitably for 1–1.5 hrs. at  $80$ – $90^\circ$ ) with solns. of alkali or alk. earth sulfides or polysulfides such as  $\text{CaS}$  or  $\text{K}_2\text{S}$ .

**Artificial rubber.** I. G. FARBERIND. A.-G. Brit. 313,440, June 11, 1928. Pastes or solid masses, which even after long storage can be disintegrated by water to a latex-like liquid, are made by cong. a latex-like emulsion or suspension of an artificial rubber-like mass (as by evapn. or centrifuging) such as may be produced from isoprene, butadiene, etc., in the presence of water and oleates such as those of Na and Mg.

**Artificial rubber.** I. G. FARBERIND. A.-G. Fr. 668,113, June 7, 1928. Artificial rubber is obtained by transforming  $\text{C}_2\text{H}_2$  prep'd. from C,  $\text{CH}_4$  or other hydrocarbons, into  $\text{AcH}$ , the latter into aldol which is reduced to 1,3-butylene glycol which is either converted by dehydration into butadiene and polymerized, or converted by partial dehydration into methyl ethyl ketone which is condensed with  $\text{CH}_2\text{O}$  to 2-methyl-3-keto-1-butanol which is reduced to 2-methyl-1,3-butylene glycol and dehydrated to isoprene. Cf. C. A. 24, 990.

**Vulcanizing rubber.** H. A. MORTON. Brit. 314,756, June 30, 1928. In vulcanizing rubber, antioxidants are used comprising 1,2-diaminoethanes in which the groups attached to the N atoms may be H, alkyl and aryl residues, mono-substituted alkyl and aryl residues and the groups attached to the C atoms of the nucleus may be H or alkyl

residues (at least one of the substituents being other than H). Examples are given of the use of: 1,2-di- $\alpha$ -naphthyldiaminoethane, 1,2-diphenyldiaminoethane and 1,2-ethylphenyldiaminoethane. These compds. do not materially affect the rate of vulcanization and may be added before or after vulcanization.

**Vulcanizing rubber.** WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,743,243, Jan. 14. Rubber is heated with a vulcanizing agent such as S in the presence of an accelerating compn. comprising the reaction product of an org. base upon the cyanogen halide deriv. of an aromatic mercaptothiazole compd., *e. g.*, the reaction product of diphenylguanidine upon the cyanogen chloride deriv. of Na mercaptobenzo-thiazole. Cf. *C. A.* 24, 266.

**Vulcanization of rubber.** COMPAGNIE FRANÇAISE POUR L'EXPLOITATION DES PROCÉDÉS THOMSON-HOUSTON. Fr. 668,110, May 16, 1928. Rubber is vulcanized with a stabilized amorphous S obtained by melting S and Se or Te (*e. g.*, S 45, Se 53 parts) and solidifying.

## Outline of Tentative Standard Laboratory Procedure for the Preparation and Physical Testing of Rubber Samples

**T**HE accompanying report on the work of the Physical Testing Committee, Rubber Division, American Chemical Society, marks the conclusion of the research work on the standardization of physical tests of rubber, which have been conducted since early in 1927, at the rubber laboratory of the Bureau of Standards, Washington, D. C., under the sponsorship of the Rubber Manufacturers Association, the Rubber Division, A. C. S., and a number of rubber companies.

The original committee was formed in October, 1926, by R. P. Dinsmore, chairman of the Rubber Division at that time. F. E. Rupert, research chemist at the Fisk Rubber Company, was chosen to conduct the research work. J. E. Partenheimer, also of Fisk, was chairman of the first committee, and was later succeeded by W. A. Gibbons, of United States Rubber Company, who in turn resigned last year and was succeeded by A. A. Somerville, of R. T. Vanderbilt Company, who has remained as chairman up to the present time.

Two progress reports were made by the committee, one on the "Importance of Temperature and Humidity Control in Rubber Testing,"\* read at the April, 1927, Rubber Division meeting at Richmond, Va., and a later report on "The Effect of Humidity and Temperature on the Ability of Rubber Compounds to Resist Abrasion," presented in September, 1927, at Detroit. This report was later amplified and released for publication in December, 1927.

**T**HE most important physical properties of rubber compounds which are usually determined in the laboratory are the tensile strength and ultimate elongation or the entire stress-strain relationship. The other physical tests which may be made are so numerous and varied that for the purpose of standardization, it is

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\*THE RUBBER AGE, Pp. 245-248, December 10, 1927.

advisable, first, to adopt uniform procedure and conditions for the entire laboratory treatment in the determination of the stress-strain relations.

*Mill Data.*—The rolls of the laboratory mill shall be 12" in width x 6" outside diameter and the working distance between the guides shall be 10½ inches. The speed of the slow roll shall be 24 R.P.M. and the gear ratio should be 1.4 or as near that figure as is compatible with engineering practice. (*Variation of 2 R.P.M. may cause 3% variation in tensile.*)

*Mill Temperature.*—No satisfactory method of controlling the temperature of the batch during mixing has been devised. However, it is recommended that the temperature of the water entering the mills be maintained at 158° F. (70° C.).

It is certain that with sufficient water passing through the rolls and a uniform initial temperature of 158° F. (70° C.), the process of mixing can be made much more uniform. It is recommended that the initial temperature of the rolls be 158° F. (70° C.) which can be attained by the flow of 158° F. (70° C.) water.

*Mill Opening.*—In order to obtain uniform mixing, it is essential that the relation between volume of batch and mill opening be such that an active bank will obtain. Since it is neither practical nor economical to standardize the size of the batch, it is recommended that the following mill openings be used with batches corresponding to the volumes in the table:

<i>Vol. of Batch</i>	<i>Distance between Rolls</i>
1200 cc. ....	.170 inch
1100 .....	.160
1000 .....	.145
900 .....	.130
800 .....	.120
700 .....	.110
600 .....	.100
500 .....	.085
400 .....	.070
300 .....	.055

*Batch Weight Tolerances.*—Weighing of all ingredients shall be accurate to within 0.25% of the weight specified. The final weight of the mixed batch and the sum of the weights taken of each ingredient shall not differ by an amount exceeding 0.6% with a compound batch or 0.3% with master batched or gum stocks.

*Mixing Procedure.*—During the period of breaking down the rubber the mill opening shall be .055" until the rubber runs smooth on the roll. The opening should then be made to correspond with the volume of the batch in the foregoing table.

The order of adding ingredients to the broken rubber shall be as follows:

*Accelerators and antioxidants*  
*Black*  
*Fillers*  
*Softeners*  
*Sulfur*

The ingredients should be incorporated as rapidly as possible. After the ingredients are in the rubber, it is recommended that the



rubber be cut 6 times, alternating first from one side and then the other. This is to be interpreted as cutting  $\frac{2}{3}$  of the way across the roll and holding until the bank just disappears. After the six cuts are made, it is recommended that the batch should be cut across and rolled six times with the roll being inserted endwise each time until the last when it should be placed lengthwise in the rolls. As soon as the bank is well balanced after this procedure, the rolls should be set to give a sheet approximately .085 inch in thickness after cooling, and the batch cut from the rolls.

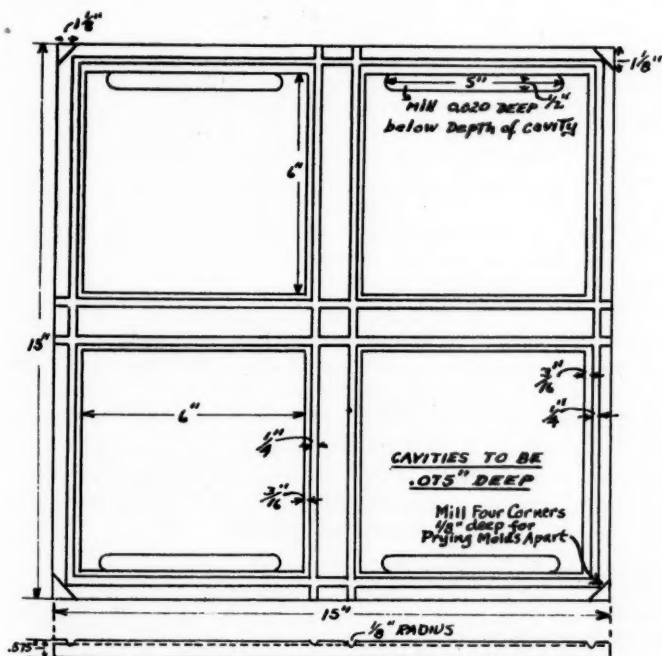


Figure 1—Design for Four Cavity Mold  
(Cover Plate to be 0.50" Thick)

*Storage of Mixed Batch.*—When cut from the rolls, the rubber compound should be laid flat upon a suitable surface (zinc, holland, talced zinc make no difference in final results) until it reaches room temperature. After cooling it may be stacked with similar batches for several hours for convenience, but for from 18 to 24 hours (either uncut or cut for curing) it should be placed on galvanized wire screens (6 mesh is convenient) to insure air circulation before curing. The storage shall be in subdued light in air having a relative humidity of 45 per cent. at 82° F. (27.6° C.). (Variations from 0 to 100% relative humidity may cause a difference of 25% in physical properties.)

*Preparation of Raw Stock for Curing.*—The uncured stock shall be cut with a die which will give an uncured slab  $\frac{1}{8}$ " less in length and in width than the corresponding dimensions of the mold cavity. The raw slabs shall be placed in the mold with the grain running parallel to the stencil.

*Maintenance of Curing Temperature.*—The specified curing temperature shall be interpreted as the inside temperature of the mold as near as it can be determined by means of a thermocouple of a mercury thermometer in a mercury well in the mold. For this can be substituted a steel block with a mercury well as described in *Ind. and Eng. Chem.*, Vol. 17, No. 5, page 535, May, 1925, in a previous report of the Physical Testing Committee.

It is recommended that to avoid cool spots in the platens due to condensed moisture, presses of the bored platen type be used. If platens of the chamber type are used, particular attention must be paid that good drainage be insured by placing the steam outlet pipe so that it is slightly below the bottom of the steam chamber.

*Timing of Cure.*—When using a platen press, the time of the cure shall start from the time the hydraulic pressure reaches its maximum and conclude at the release of the hydraulic pressure. The slabs shall be removed from the mold immediately after the conclusion of the cure.

*Mold Dimensions.*—The depth of the cavity for the rubber slab shall be .075 inch. The thickness of the steel mold under the cavity and the thickness of the cover plate shall be .50 inch. The mold shall be of such dimensions that the slab while curing shall not be nearer than three inches from the edge of the platen. A drawing for a recommended mold is shown in Fig. 1.

*Temperature of Molds.*—The mold shall be brought to temperature before inserting the uncured stock by being placed in the closed press for a period of not less than 20 minutes.

*Shielding of Molds.*—During the curing the molds shall be protected from draughts by the use of wooden ells or shields of some sort. (*Protection often causes a rise of 1° C. in temperature of mold.*)

*Cleanliness of Molds.*—No preparation of any sort shall be used on the molds to prevent sticking. The molds shall be kept clean and it is recommended that they be cleaned as soon as there is a tendency of the cured stock to stick.

It is suggested that the molds may be cleaned, using any one of the following:

- (a) Ground emery and water;
- (b) Buffer cloth;
- (c) Whiting paste.

*Cooling of Cured Slabs.*—When the slabs are removed from the molds they shall immediately be placed in water to cool for a minimum time of ten minutes. This water, if kept in a retainer, should be changed frequently to prevent contamination. When removed from the water, the slabs shall be wiped dry and placed upon a liner or wire screen for storage in subdued light.

**Dieing of Specimens.**—When the specimens are cut, it is recommended that the die or the stock be wet with water. Any residual water shall be wiped from the test pieces before conditioning for testing.

**Standard Die.**—The die used shall be the one illustrated in Fig. 2. The width of the constricted portion of the die shall be  $0.250 \pm .005$  inch and great care shall be taken when the die is resharpened that these dimensions are maintained. It is essential that the cutting edge of the die be kept sufficiently sharp and free from imperfections so that the died specimen may have a smooth cut surface with a minimum of concavity.

**Conditioning for Testing.**—The test specimens shall be conditioned for 24 hours in air with a relative humidity of 45% at  $82^{\circ}$  F. ( $27.6^{\circ}$  C.) before testing at the same temperature.

**Measurement of Test.**—In measuring the thickness of a test specimen, the diameter of the presser foot shall be 0.25 inch, and it shall be actuated by a dead weight of 3 ounces. The average thickness of the specimens in the constricted portion shall be used in the determination of the stress-strain relation and the tensile at break. The width of the test specimens shall be considered as the width of the die.

**Bench Marks.**—Bench marks, 1 inch apart, shall be placed near the center of the constricted portion with an instrument as illustrated and used for determining the per cent. elongation.

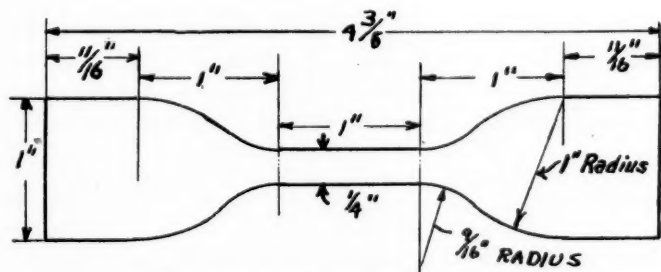


Figure 2—Die for Rubber Testing

**Temperature of Testing.**—The testing shall be done at a temperature of  $82^{\circ}$  F. ( $27.6^{\circ}$  C.) and this should be controlled within plus or minus 2 degrees. (A variation of  $1^{\circ}$  C. may cause a 1% difference in tensile or modulus.)

**Speed of Testing.**—The testing shall be done with a machine which stretches the specimen at a speed closely comparable to that attained by using a Scott Tester whose lower grip travels at the rate of 20 inches per minute. (Slight errors may be caused by varying this speed.)

**Evaluation of Results.**—Breaks which occur outside of the straightaway portion of the specimen shall be discarded. In recording the final tensile of a compound obtained by three or more indi-

vidual tests, it is recommended that the highest figure, and those that come within five per cent. of this value be averaged, discarding those results which vary more than 5% from the highest tensile figure.

# Moisture Content of Carbon Blacks\*

By WILLIAM B. PLUMMER

*General Atlas Carbon Company, New York, N. Y.*

A METHOD for the determination of total moisture in carbon blacks recently proposed (1) involves mixing the sample (5 grams) with 25 cc. of dry xylene and 200 cc. of dry mineral oil, heating to 175° C., passing dry nitrogen through the system until the xylene and water have been displaced from the carbon black-oil mixture, and continuing the nitrogen stream until all water has been displaced from the intermediate xylene receiver and absorbed in the final  $\text{CaCl}_2$  tubes. By this method values of 3.54-5.96 per cent. total water are obtained for channel blacks, whereas the same samples showed only 1.42-1.85 per cent. loss on ordinary drying for 6 hours at 105° C.

The moisture content of carbon blacks is an important factor in many of their uses, so that the discrepancy between this and the usual oven drying method becomes a matter of practical importance as well as theoretical interest. Hence it has been further investigated.

Various types of blacks on heating in a 1-2 mm. vacuum show widely differing weight losses, as illustrated by the results in Table I.

BLACK	Table I		
	Loss in Weight at 450° C.	750° C.	950° C.
	Per cent.	Per cent.	Per cent.
High yield black	0.68	1.12	1.61
Channel black	2.45	5.13	7.23
Roller black	3.59	9.09	15.94

†Based on original material air dry only.

Evidently it is necessary to go to 750° C. vacuum heating to obtain a loss with channel black equal to that shown by the xylene-oil

\*Reprinted from the Analytical Edition, *Industrial and Engineering Chemistry*, January 15, 1930.



method (1) at 175° C., which is possible but would be surprising.

Certain of Johnson's (3) results bear directly on this question. Johnson heated various samples of black at 950° C. (atmospheric pressure) and analyzed the gases evolved. In parallel determinations dry nitrogen was passed through the heating chamber and the H<sub>2</sub>O evolved was determined by absorption in CaCl<sub>2</sub> tubes. In Table II his moisture results are shown and the calculated total mols of C, H<sub>2</sub>, and O<sub>2</sub> evolved in all gaseous forms are given.

Table II

BLACK	FREE	COM- BINED	GAS IN DRY GAS GIVEN			MOL RATIO
	H <sub>2</sub> O AT 105° C.	H <sub>2</sub> O AT 105° C.	OFF AT 950° C.	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> :O <sub>2</sub> IN DRY GAS AT 950° C.
	Per cent	Per cent	Mols	per 100	grams	original black
Channel A	1.35	0.30	0.132	0.051	0.078	0.65
Channel B	2.71	0.44	0.190	0.080	0.113	0.71
Roller D	2.92	0.44	0.275	0.111	0.174	0.64
Roller E	4.32	0.72	0.365	0.042	0.236	0.18

The H<sub>2</sub> to O<sub>2</sub> ratio is the most important result given in Table II. The evolved gas was found by Johnson to contain CO<sub>2</sub>, CO, H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, N<sub>2</sub>, and "illuminants." *A priori*, it would not be impossible for such a gas to have been formed by synthetic reactions during the heating process, with H<sub>2</sub>O and C as the only starting materials. If this were the case, however, the final H<sub>2</sub> to O<sub>2</sub> ratio, regardless of the actual components, would obviously be 2.0, which is far from being the case. This shows conclusively that the observed weight loss does not merely represent loss of moisture plus its "water gas" reaction with the carbon. It shows the original presence either of O<sub>2</sub> as such, or of oxygen combined with carbon and hydrogen in compounds where the molecular H<sub>2</sub> to O<sub>2</sub> ratio is very much less than 2.0.

Because of these facts the xylene-oil method (1) was studied further to determine possible causes of error. It has been found that on bubbling ordinary commercial nitrogen containing 0.3 per cent of oxygen through mineral oil at 175° C. an apparent conversion of about 60 per cent. by weight of the oxygen to water is obtained. With purified "O<sub>2</sub>-free" nitrogen bubbled through the oil only a small blank is obtained. On the other hand, if thoroughly oven-dried carbon black be added to the oil and "O<sub>2</sub>-free" nitrogen passed through, the water evolved is equivalent to about 1 per cent., based on the black. Similarly, using black previously heated in vacuum at 1000° C., cooled in vacuum, and saturated with dry O<sub>2</sub> at 25° C., the water evolved equals 1.45 per cent. on the black.

#### Experimental Work

A train was set up in which commercial tank nitrogen (0.3 per cent. oxygen) was passed through two CaCl<sub>2</sub> towers and bubbled

through 500 cc. of "straw oil" held at 175° C., through an oil trap (a cotton-filled U-tube held at 100° C.), through two CaCl<sub>2</sub> absorption tubes, through a protective CaCl<sub>2</sub> U-tube, and through a standard "wet-test" gas meter (0.1 cubic foot dial). A total of 42 liters (1.5 cubic feet) of nitrogen was passed through the oil at a rate of 17 liters (0.6 cubic foot) per hour. The oil flask was then by-passed and 28 liters (1.0 cubic foot) more passed through to sweep out the apparatus (Table III). Following this a blank was run in which the nitrogen from the tank was passed through three bubbler bottles containing alkaline pyrogallol solution held at 60-70° C. before passing through the CaCl<sub>2</sub> towers and the oil. Another duplicate run was then made, using the same volumes, with purified "O<sub>2</sub>-free" nitrogen, but with 10 grams of thoroughly oven-dried channel carbon black mixed with the oil.

The foregoing determinations of H<sub>2</sub>O absorbed are not exact, as, in order to maintain parallelism with the xylene-oil method, the CaCl<sub>2</sub> tubes were not saturated with CO<sub>2</sub> before the determination. The first run, therefore, was repeated, using unpurified nitrogen, but replacing one of the preliminary CaCl<sub>2</sub> towers with a soda lime tower and saturating the CaCl<sub>2</sub> absorption tubes with CO<sub>2</sub> before the test. Using the same quantities of nitrogen, etc., the H<sub>2</sub>O found was about 10 per cent less than in the first run. This illustrates the magnitude of this error. Comparison of the present experiments with the xylene-oil method, however, should preferably be based on the similar condition of CaCl<sub>2</sub> tubes not saturated with CO<sub>2</sub>.

In the final run purified nitrogen and saturated CaCl<sub>2</sub> tubes were used, and 34 grams of channel black, treated as follows, were added to the oil. The black had been heated for 2 hours at 1000° C. and 1 mm. pressure, cooled in vacuum, saturated with dry oxygen at room temperature, and introduced into the oil flask without contact with air. Periodic weighings showed an initial rate of H<sub>2</sub>O evolution of about 0.200 gram per hour, falling regularly over a 6-hour period to a constant value of 0.004 gram per hour, which corresponds with the blank obtained in the second run.

In all of these tests the oil was first dried by heating to 250° C.

Table III

RUN	BLACK USED	WEIGHT OF BLACK	NITRO-GEN	CaCl <sub>2</sub> SATURATED WITH CO <sub>2</sub>	TIME	APPARENT H <sub>2</sub> O	
		Grams			Hours	Gram	% of black†
1	None	....	0.3% O <sub>2</sub>	No	2.5	0.1245	....
2	None	....	Purified	No	2.5	0.0115	....
3	Oven-dried	10	Purified	No	2.5	0.0784	0.67
4	None	....	0.3% O <sub>2</sub>	Yes	2.5	0.1122	....
5	Degassed and saturated with O <sub>2</sub>	34	Purified	Yes	6.5	0.5164	1.45

†After deduction of corresponding blank.

while passing dry nitrogen through the flask during the heating and cooling period.

### Discussion

The foregoing data show conclusively that oxygen in the nitrogen or adsorbed on the black may react with mineral oil under the test conditions. In the description of the xylene-oil method the duration of the test and the purity and volume of the nitrogen used are not stated. It is understood, however,<sup>1</sup> that the nitrogen was of high purity, that it passed over but not into the oil, and that all  $H_2O$  was evolved from the oil-black-xylene mixture in 10-30 minutes. This practically eliminates the nitrogen as a factor in the results, but the present data show the need for precautions on this point. It therefore seems probable that oxygen adsorbed on the black is the main factor. The rate of reaction observed in run 5, using 34 grams of black, might appear to be too low to account for the  $H_2O$  evolved in 10-30 minutes in the xylene-oil method using only a 5-gram sample. However, the kinetics of reactions in a liquid-solid-adsorbed gas system are so complex that it is difficult to predict the effect of the amount of solid present on the observed reaction velocity, while also this must depend largely on the particular character of the oil used. In the present case the oil was a refined paraffin wash oil ("straw" oil) and presumably more resistant to oxidation than the average petroleum fraction of like boiling range.

Based on the apparent conversion of  $O_2$  to  $H_2O$  observed in run 1, the 0.67 per cent.  $H_2O$  evolved in run 3 would correspond to 1.0 per cent. oxygen adsorbed on the black, and the 1.45 per cent.  $H_2O$  found in run 5 would correspond to 1.9 per cent. oxygen. The work of Hulett and Cude (2) shows only about 0.14 per cent. free  $O_2$  removable as such from channel blacks at room temperature and 0.6-1.0 per cent. removable as  $O_2$ ,  $CO_2$  and  $CO$  at  $445^\circ C$ , while their original analysis shows about 2.5 per cent. total oxygen present. Johnson's results (3) show about 3.0 per cent. oxygen removable in all forms (except  $H_2O$ ) at  $950^\circ C$ . No final conclusions can be drawn from these figures as to the original amount of adsorbed  $O_2$ , but from what is known of the mechanism of adsorption of  $O_2$  on carbon and other oxidizable surfaces, and of the mechanism of its subsequent removal (Langmuir's general studies on oxygen films), it is probable that a large proportion of the total oxygen content is originally present as adsorbed  $O_2$ , regardless of the form in which it ultimately appears on heating and evacuating.

All of the foregoing experimental observations and general facts are in agreement with the belief that the "additional moisture" shown by the xylene-oil method is mainly the product of the reaction of the mineral oil with the oxygen adsorbed on the black.

### Acknowledgment

These results are published with the permission of the Combustion

tion Utilities Corporation, at whose laboratories, at Linden, N. J., the work was carried out.

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<sup>1</sup>Private communication from Carson.

#### Literature Cited

- (1) Carson, *Ind. Eng. Chem., Anal. Ed.*, **1**, 225 (1929).
- (2) Hulett and Cude, *Bur. Mines, Bull.* **192**, 76 (1922).
- (3) Johnson, *Ind. Eng. Chem.*, **20**, 904 (1928).

# The Question of Vulcanization Without Sulfur\*

Experiments on Hot Vulcanization and Vulcanization in Ultraviolet Light with the Aid of  
1, 3, 5-Trinitrobenzene and Picric Acid

By F. KIRCHHOF

## Vulcanization With Heat

**T**HIS subject has been previously treated by L. Eck.<sup>1</sup> The present article contains merely the results of a few experiments, which, as might be anticipated, seem suited to assist but little the progress of sulfur's new rivals.

We recall that Ostromislensky<sup>2</sup> is said to have succeeded in obtaining vulcanizates of technical value by means of nitro-compounds, especially 1, 3, 5-trinitrobenzene, in the absence of sulfur or any substance forming sulfur.

It is difficult to obtain the trinitrobenzene (TNB for short) recommended by Ostromislensky, as it apparently has not been manufactured in Germany since the end of the war. The first experiments were therefore carried out with the analogous compound, 2, 4, 6-trinitrophenol, in which the nitro groups are in the same symmetrical position as in TNB, and which is more frequently met with under the name of picric acid. The percentages given by

\*Translated by J. P. Fahy from *Gummi-Zeitung*, Vol. 44, No. 5, pp. 252-253, Nov. 1, 1929.



Ostromislensky were used, and also the accelerators, or more properly activators, litharge and carbon black.

A mixture consisting of

	Parts by weight
Brown crepe .....	100
Litharge .....	30
Picric acid .....	0.5

was stored for several days and then press-cured at 140°C. The mass remained soft and tacky, and showed no indication whatever of vulcanization.

A second mixture which contained in addition to the above ingredients twenty-five parts by weight of American gas black was heated under the same conditions as the first with the following results:

60 min. at 140°C—weakly vulcanized

120 min. at 140°C—more strongly vulcanized

The addition of gas black therefore seems to play an essential role, and litharge alone, which is so effective in sulfur vulcanization, has in this case a retarding or depolymerizing effect.

Among the "vulcanizates" thus obtained there are none that may be considered as similar to the vulcanizates obtained with sulfur. On the contrary, tough, leathery, inelastic products resembling reclaim are obtained, which have but one characteristic in common with sulfur-vulcanizates, viz., insolubility in rubber solvents. It may be remarked that the second mixture before heating was completely soluble in benzene despite its high content of gas black, while the heated samples retained their shape and swelled but little after lying for weeks in benzene.

Since this swelling characteristic is indicative of vulcanizates only "in the broadest sense" (even reclaim shows it), then it alone is not sufficient reason for classifying the products obtained by Ostromislensky's method as "vulcanizates" without further ado. Their physical properties, such as toughness, are not to be ignored, but their elasticity and extensibility leave much to be desired. In this respect also they resemble low grade black reclaim, and at best can only be called "pseudo-vulcanizates."

It might be objected that 2, 4, 6-trinitrophenol (called TNPh for short) might not have the same effect as TNB. After some effort the author succeeded in obtaining a few tenths of a gram of this costly material, and the above experiments were repeated with it.<sup>3</sup> Because of the small quantity of substance available, the experiments could only be carried out with rubber solutions. To a 25% solution of Para rubber in benzene there was added a concentrated benzene solution of TNB, corresponding to 1% TNB on the rubber content.

To this base there was now added:

- a) litharge 30 parts by weight to 100 of rubber
- b) gas black 30 parts by weight to 100 of rubber
- c) Equal amounts of a) and b) were mixed.

The solutions were poured on glass plates, and allowed to dry completely, warming gently. The films thus obtained were about

0.5 mm. thick, and were heated in an air oven at 140°C. for 30, 60, and 120 minutes respectively.

The results were as follows:

Compound	Cure in minutes	Appearance of film
Base mix	60	Surface dry, but mass unvulcanized.
	120	Surface tacky, mass unvulcanized.
a) ditto + PbO	60	Surface markedly tacky, mass unvulcanized.
	120	ditto
b) ditto + gas black	60	Surface not tacky, mass unvulcanized.
	120	ditto
c) ditto + PbO + gas black	30	Surface dry, mass weakly vulcanized
	60	ditto
	120	Mass slightly tacky.

It is interesting to observe that a "surface vulcanization," indicated by the disappearance of tackiness, could be noted only in the base mix. The litharge-gas black mix is not considered, as gas black alone causes a dry surface. The mix containing litharge alone showed clear signs of depolymerization on the surface as well as in the interior, as in the case of the TNPh mix.

Therefore in the presence of the nitro compounds, TNB and TNPh, litharge has no accelerating action such as it possesses in sulfur mixes. The changes effected by these nitro compounds cannot be identified with sulfur-vulcanization without further ado.

To all appearances the changes in the rubber observed by Ostromislensky belong in the great category of those isomeric transformations brought about by sulfuric acid, sulfo-acids, sulfur chloride, etc., as described by Kirchhof, Fisher, and others.<sup>4</sup> Such changes can even take place to some extent in sulfur-vulcanization, probably especially in the case of reversion or overcure and in reclaiming sulfur-vulcanizates. At any rate the products obtained resemble physically those produced by cyclicizing agents or by the nitro compounds of Ostromislensky.

### Vulcanization With Ultraviolet Light

It was interesting to see if TNB and TNPh behaved like sulfur under the influence of ultraviolet light. For this purpose twenty per cent solutions of Para rubber were mixed with one to three per cent of the nitro compound, and evaporated to dryness on polished quartz plates. When the films thus obtained were completely dry, they were exposed, either directly or hermetically covered by a second quartz plate, to the action of a quartz lamp (220 v., 2 amp.) at a distance of 15 cm. (Temperature 65°C.)

The rubber film containing 3% TNPh was completely dry on the surface after one hour's illumination and had a slight metallic shimmer, whereas an unprotected rubber film without TNPh exposed for an equal length of time became extremely tacky on the surface. The TNPh film also showed some elasticity and extensibility and had become quite insoluble in benzene, even when the

effect of the ozone which was formed was excluded by covering the film with a second quartz plate.

Still more striking was the change in the film containing 1% TNB. The latter became intensely brownish-yellow and clear as glass after exposing each side of a film between two quartz plates for one hour. It showed good elasticity and an elongation of 600 to 700%, but part which was exposed on one side was weakened by oxidation and showed an elongation of only 400 to 500%. These vulcanizates therefore are clearly different from those obtained by heating as above described. However, they may have no practical importance.

Through the researches of Porritt and Asano<sup>5</sup>, it has been shown that rubber in solution or in a thin film is transformed by short-wave ultraviolet light into what is probably an isomeric form (called by Kirchhof, photo-cyclo-rubber). This change is strongly accelerated by certain substances such as white phosphorus and selenium<sup>6</sup>, as evidenced by the gel formation of the solution.

Probably the vulcanization by light of mixtures containing sulfur discovered by Bernstein in 1912 belongs to this class, as a form of sulfur activated by the ultraviolet light has an analogous accelerating action on the transposition and the combination with sulfur of the rubber which is depolymerized by the ultraviolet light.

The effectiveness of ultraviolet rays depends upon the transparency of the irradiated substance. Rubber itself, especially in a thin layer, is quite permeable to ultraviolet light<sup>7</sup>, but any change in its transparency through the addition of fillers would have a marked effect on the intensity of the change produced by ultraviolet light. Picric acid with its strong yellow color makes a film of rubber 0.1 mm. thick completely impermeable to ultraviolet light, but a film of rubber 0.4 mm. thick containing 1% TNB remains completely permeable. This permeability completely disappears during the irradiation, even in the case of films covered with quartz plates where oxidation is excluded. A film of pure rubber irradiated for two hours and also a film of rubber containing 1% TNB which was heated for two hours in an oven at 140°C. showed no change in their permeability to ultraviolet light. This phenomenon in the case of a film containing TNB is accordingly wholly analogous to the displacement of the absorption boundary for ultraviolet light observed in sulfur-vulcanization, which parallels the chemical combination with the sulfur<sup>8</sup>, as indicated by the saturation of the double bonds. Hence, of course, the effect of TNPh in the presence of ultraviolet light is also limited to the surface only, as its marked absorptive power prevents the penetration of active rays to deeper layers<sup>9</sup>.

In conclusion the results obtained with the nitro compounds TNB and TNPh may be formulated as follows: The "hot vulcanizates" obtained with these substances in the presence of considerable quantities of gas black, which apparently acts as a necessary surface catalyst, have a physical resemblance to reclaim or certain cyclo-rubbers, and may also resemble them chemically. Hence they can only be spoken of at best as "pseudovulcanizates."

The ultraviolet vulcanizates first observed by Kirchhof possess an essentially different behavior, especially those containing TNB,

resembling cold cures physically, and chemically, too, in so far as they are analogous to the latter or even to sulfur-vulcanizates in showing marked absorption of ultraviolet light even in a thin film, thus indicating the saturation or transposition of the double bonds in the rubber hydrocarbon molecule<sup>10</sup>.

### Notes

- (<sup>1</sup>) *Gummi-Ztg.* **43**, 2481 (1929).
- (<sup>2</sup>) *India Rubber World*, **80**, 55 (1929); *Gummi-Ztg.* **42**, 2378 (1929).
- (<sup>3</sup>) This was obtained through the courtesy of Dr. W. Esch. It was identified as 1, 3, 5-trinitrobenzene by its melting point of 119-120°C., its crystal form and its solubility. The crystalline form of both nitric compounds (monoclinic and rhombic) are remarkably similar to that of sulfur; also their melting points (121°C. and 122°C. respectively) lie close to that of sulfur (S mon. = 119°C.).
- (<sup>4</sup>) *Kautschuk*, **2**, 1 (1926); **4**, 142 (1929).
- (<sup>5</sup>) *Kautschuk*, **3**, 239 (1927).
- (<sup>6</sup>) *Kautschuk*, **3**, 28 (1927).
- (<sup>7</sup>) *Gummi-Ztg.* **43**, 22 (1929).
- (<sup>8</sup>) *Ind. Eng. Chem.* **17**, 808 (1925).
- (<sup>9</sup>) The photographs taken will be published later.
- (<sup>10</sup>) Apparently in these chemical changes the nitro groups are strongly disrupted (reduction and addition to the double bonds of the rubber hydrocarbon?); this would explain among other things the intense yellowish-brown color of the films after irradiation, as TNB and TNPh irradiated alone show no change in intensity of color.

# Vulcanization of Rubber

By

*Organic Peroxides or by Ammonium  
Persulphate*

By Iwan Ostromislensky<sup>1</sup>

THE fact that rubber may be vulcanized by means of various organic peroxides in the entire absence of sulphur was shown by the writer as early as 1915. In these experiments, benzoyl peroxide, peracetic or perphthalic acid, and triphenylmethyl peroxide were used. It was also observed that the oxygen in the air will easily oxidize synthetic or purified natural rubber at room temperatures, gradually transforming it into solid and sometimes ebonite-like compounds. These compounds, which very likely have the structure of highly molecular peroxides or oxides, etc., will likewise vulcanize rubber in the absence of sulphur.<sup>2</sup> Our experience indicates that vulcanization of rubber by means of the above mentioned peroxides takes place much more rapidly and easily, i.e., at a lower temperature than is usually employed in sulphur cures. It is astonishing to learn that these peroxides will vulcanize rubber not only in the absence of sulphur but likewise without the admixture of any foreign substances, such as metallic oxides or accelerators of any kind, etc.

As a curiosity it should be mentioned that mixture A made up of 100 gms. of rubber and 30 gms. of benzoyl peroxide<sup>3</sup> vulcanizes completely in one to two minutes at 13 pounds pressure (corresponding to 119° C.) and yields a soft rubber.

According to Twiss, benzoyl peroxide does actually vulcanize rubber in the absence of sulphur, but the product differs considerably from commercial products cured with sulphur or sulphur chloride.<sup>4</sup> However, *when a sufficient*

<sup>1</sup>Formerly professor of organic chemistry, University of Moscow, Moscow, Russia.

<sup>2</sup>J. Russ. Phys. Chem. Soc., 47, 1467, and 1904 (1915). For reviews of this article see J. Soc. Chem. Ind., 35, pp. 59, 370 (1916). Chem. Abstracts, 10, pp. 1946, 3177 (1916); Caoutchouc & gutta-percha, 16, p. 9701 (1919); J. Chem. Soc., London, 110-i, p. 178 (1916); INDIA RUBBER WORLD, 54, p. 535 (1916); Chem. Zentralblatt, 1916, I, 955; Gummi-Zig., 30, 1102 (1916); Z. angew. Chem. 30, II, 48 (1916). Benjamin T. Brooks, "The Chemistry of the Non-Benzenoid Hydrocarbons and Their Derivatives," p. 137, New York, 1922.

<sup>3</sup>During the milling process the benzoyl peroxide should be added in comparatively small quantities and be spread over as large a surface of rubber as possible.

<sup>4</sup>J. Soc. Chem. Ind., 782 (1917). Compare, King, Met. Chem. Eng., 15, p. 231 (1916), also Benjamin Brooks, *Ibid.*, p. 137.



*amount of benzoyl peroxide was used*, no essential difference in these products could be detected.

Mixture B of 100 gms. of rubber and 7 gms. of benzoyl peroxide vulcanizes in 25 minutes at 40 pounds pressure. The resulting product is of little value, but it is worth while remarking that the vulcanizate is so soft that, when stretched, it breaks in the jaws of the machine. Therefore its tensile strength fluctuates widely and within a quite unusual range, namely, between 1,430 and 430. The set is 0.08 and the stretch 9.6. After being heated in the usual way (3 hours at 235° F.), it showed the following constants: tensile, 666, 667, and 673 pounds per square inch, set, 0.05 inches, and stretch, 9.0 inches.

As a matter of fact the product obtained from compound B differed appreciably from commercial products cured with sulphur. For, regardless of its constants, it is easily milled under usual conditions, loses its form in this process and becomes, like crude unvulcanized rubber, a homogeneous plastic mass. Experience has shown that the minimum quantity of benzoyl peroxide to be used as a vulcanizing agent is 10 per cent. (reckoned on the amount of the original rubber).

Mixture C, consisting of 100 gms. of rubber and 10 gms. of benzoyl peroxide, vulcanizes completely in 10-15 minutes at 13 pounds pressure. The product possesses good properties; it is transparent, although somewhat sticky at first. After some time its surface becomes covered with small shining snow-white crystals; at the same time it loses its stickiness. The crystals which separate out may be easily removed by immersing the substance in methyl alcohol for several hours, whereupon it again becomes quite transparent, although somewhat sticky. This stickiness disappears in 2 or 3 days, probably owing to traces, undetected by the eye, of the white crystals that separate out and act somewhat in the same manner as talcum.<sup>5</sup> The constants averaged: tensile, 1,540 pounds, set, 0.09 inches, and stretch, 10 inches.

In Moscow some years ago the writer noticed that the rubber products vulcanized by means of various peroxides were gradually and sometimes even rapidly transformed into a very sticky and viscous mass, losing their original shape in the process. This peculiarity is precisely what marks the difference between this product and rubber cured with sulphur and nitro compounds. Experience has shown that neither aromatic amines nor the oxides and sulphides of metals, nor yet tannic acid, can protect against such decomposition of these products. Moreover, they are likely to

<sup>5</sup>There is every reason to presume that the nonsticky condition of the surfaces of rubber vulcanized under ordinary conditions with sulphur is likewise due to a secretion of a larger or smaller amount of sulphur dust on the surface, which dust is at times invisible to the eye. Without any doubt traces of this sulphur react on the surface of the vulcanizate in the same way as does talcum.

lessen their resistance to rupture quite considerably. And yet vulcanization of rubber by means of peroxides is most interesting not only from a theoretical but from a practical standpoint, for the procedure may lead to the production of transparent and almost colorless elastic products.

For this reason endeavor was made to find a substance which would protect these vulcanizates from decomposition and thereby stabilize them. Such a product, according to observations, is sulphur. The necessary amount of this substance should be within the limits of 0.2 to 1 per cent or more. In contradistinction to sulphur, selenium and tellurium will not prevent decomposition of rubber vulcanized by means of peroxides.

Mixture D, consisting of 100 gms. of rubber, 10 gms. of benzoyl peroxide, and 1 gm. of sulphur, vulcanizes completely in 15 minutes at 13 pounds pressure. In respect to constants, the resulting product is scarcely different from mixture C, which does not contain any sulphur at all. Its tensile is 1,620 pounds, set 0.09 inches, and stretch 10.5 inches. But, in contradistinction to mixture C this product can be stored for quite a long time without undergoing any change, and it resembles sulphur-cured rubber. Approximately ten days after vulcanization the rhombic modification of sulphur begins to recrystallize out of it. If, however, the vulcanization of mixture D is prolonged thirty minutes at 13 pounds pressure or 10 minutes at 40 pounds pressure, it results in a stable solution of sulphur in the rubber.

A magnificent result is obtained in the vulcanization of rubber by means of benzoyl peroxide in the presence of a larger quantity of sulphur.

Mixture E was made up of 100 gms. of rubber, 10 gms. of peroxide, and 10 gms. of sulphur. It was then vulcanized for 25 minutes at 13 pounds pressure. The constants averaged before heating, tensile 3,025 pounds, stretch 10.5 inches, and set 0.13 inches; after heating (3 hours at 235° F.), tensile 2,605 pounds, stretch 10.7 inches, and set 0.18 inches. This product is white in color and resembles the vulcanizate obtained by means of zinc oxide and sulphur. It is absolutely nonsticky. In our opinion vulcanizate E may be used for such articles as must be free from heavy metals or their oxides, litharge, zinc oxide, magnesia, etc., or in cases where the product used is required to give an unusually good stretch, or when the rubber substances must be relatively softer and more elastic.

Although it is hardly credible, yet it could have been foretold *a priori* that the active agent which vulcanizes the rubber in mixture E is precisely sulphur and that benzoyl peroxide only accelerates the process or reduces its temperature. However, experiments did not corroborate these suppositions. It appeared that benzoyl peroxide in itself does not accelerate ordinary sulphur cures of rubber to any

appreciable extent.<sup>6</sup> Thus, efforts were not successful in obtaining a vulcanizate from mixture F, made of 100 gms. rubber, 6 gms. sulphur, and 0.3 to 0.5 gms. of benzoyl peroxide, either at 13 or 40 pounds pressure in 2 hours of vulcanization. On the other hand, rubber containing 10 per cent. of sulphur, when vulcanized at 13 pounds pressure, does not show any traces of vulcanization even after 1 hour's heating; whereas mixture C containing 10 per cent. benzoyl peroxide vulcanizes completely without sulphur in 10 minutes at the same pressure, and greatly resembles mixture E. Lastly, a characteristic physical property of vulcanizate E points directly to the fact that in this case the active vulcanizing agent is precisely benzoyl peroxide and not sulphur. For, from rubber containing 20 per cent. of foreign substances it has not, so far as known, been possible to obtain a vulcanizate with the high stretch displayed by mixture E (10.5) at a tensile of 3,025 pounds. Yet such constants together with high resiliency and softness<sup>7</sup> are characteristic for rubber vulcanized by means of peroxides, irrespective of whether or not the process was conducted in the presence of sulphur or without it.

Vulcanization by benzoyl peroxide cannot be conducted in the presence of metallic oxides, at any rate in the presence of litharge. When stored, these vulcanizates decompose very quickly and are transformed to viscous and sticky masses. Metallic aluminium powder likewise accelerates the decomposition of rubber vulcanized with benzoyl peroxide. It also destroys the action of the sulphur used in the process.

Mixture G was made up of 100 gms. rubber, 10 gms. benzoyl peroxide, 10 gms. sulphur, and 20 gms. aluminium powder. It became sticky in some 15 to 20 days after vulcanization (20 minutes at 13 pounds pressure).

In conclusion the writer desires to mention that he has some samples of rubber which were vulcanized with 10 per cent. benzoyl peroxide three years ago, which are very well preserved. These samples are more homogeneous (being free from the brittle and hard layer which usually covers the surface), and they display higher tensile and stretch than samples made of a mixture of 100 gms. rubber, 10 per cent. sulphur, and 10 or 15 per cent. zinc oxide, which were vulcanized at the same time.

It was also observed that ammonium persulphate will

<sup>6</sup>The writer is satisfied that the vulcanization of rubber by means of benzoyl peroxide not only is not accelerated but is actually somewhat retarded by the action of sulphur. In the same way the presence of benzoyl peroxide does not produce any appreciable effect on the speed of vulcanization when the latter is conducted by means of nitro compounds. For example, a mixture of 100 gms. of rubber, 3 gms. of meta-nitrobenzol, and 30 gms. of zinc oxide is completely vulcanized in 60 minutes at 40 pounds pressure, both in the presence and in the absence of 2 gms. benzoyl peroxide.

<sup>7</sup>This constant was measured in the usual way by ascertaining the height of rebound of a metal ball falling from a definite height onto a rubber sheet made of this vulcanizate.

vulcanize rubber, yielding, however, a product which is porous, brownish in color, and in general of little value. Apparently, in vulcanization there occurs an evolution of some gas, the nature of which has not yet been established ( $\text{SO}_2$  or  $\text{NH}_3$ ). A mixture of 100 gms. rubber and 25 gms. persulphate is completely vulcanized in  $2\frac{1}{2}$  hours at 45 pounds pressure. The addition of some calcium oxide to the original mixture will not prevent the evolution of this gas, and ultimately a sticky product of still less value is obtained. The addition of 22 per cent. of lamp black will somewhat improve the properties of the vulcanizate. Activated carbon or clay might absorb most of the gas evolved in this process.

### Summary

1. Organic peroxides vulcanize rubber not only in the absence of sulphur but likewise without any foreign substances such as metallic oxides or accelerators of any kind.
2. Rubber vulcanized by means of an adequate amount of benzoyl peroxide (10 to 30 per cent.) gives a soft rubber product which does not differ in point of physical properties from products cured with sulphur, or rather with sulphur chloride.
3. The process of vulcanizing rubber with benzoyl superoxide is completed in a relatively short time even at a fairly low temperature, sometimes even in two minutes at  $119^\circ \text{C.}$ , corresponding to 13 pounds pressure.
4. Vulcanization of rubber by means of peroxides may lead to the formation of a soft, transparent and elastic product, which is almost entirely colorless.
5. The products in question vulcanized by means of various peroxides are gradually converted to a very sticky and viscous mass.
6. Sulphur protects the vulcanizates in question from such decomposition or oxidation. However, the products obtained in vulcanization of rubber with organic peroxides in the presence of sulphur are opaque.
7. As distinguished from sulphur, selenium, tellurium, their sulphides, metal oxides (in particular, lead oxide) as well as amines (aniline), tannic acid, and metallic aluminium powder not only do not protect the peroxide vulcanized rubber products from decomposition or oxidation but, on the contrary, they accelerate such processes quite considerably.
8. Benzoyl peroxide is the active vulcanizing agent in the process of heating rubber with a mixture of sulphur and benzoyl peroxide.
9. When rubber is subjected to the action of a mixture of some nitrobenzenes and benzoyl peroxides, vulcanization is effected exclusively by the nitrobenzenes, and the benzoyl peroxide remains altogether passive.
10. Ammonium persulphate vulcanizes rubber completely,

resulting in a porous product which, generally speaking, is of small practical value.

### Acknowledgment

The work described in this article was performed in the General Laboratories of the United States Rubber Co., New York, N. Y. I take this opportunity to acknowledge to Ernest Hopkinson and to A. E. Jury my appreciation for the interest which they invariably showed in the work and for the arrangements they made for conducting these researches.



# A Spiral Model of Rubber<sup>1</sup>

H. Fikentscher and H. Mark

As a result of the work of Harries, the synthesis of rubber-like substances and the recent X-ray researches of Katz and of Hauser and his collaborators,<sup>2</sup> one is justified in regarding the isoprene residue as the basis of the structure of rubber. The reason it has not been possible to obtain quite 100 per cent. of isoprene from rubber, in the way that cellulose can be converted quantitatively into its parent substance, glucose, is because of the strength of the C-C bonds of the individual isoprene residues of the rubber compared with the more easily cleaved glucoside oxygen bridges in cellulose. Above all, the extraordinarily thorough investigations of Staudinger and his collaborators have contributed important facts about the general behavior of chain-forming molecules, the application of which to rubber leads to the conviction that rubber contains long chains held together by primary valences, called macromolecules by Staudinger, a view which was held by Pickles years ago (cf. Dittmar, *Der Kautschuk*, 1912).

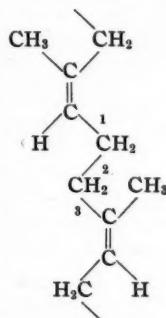
Utilizing the Bragg numbers for the diameter of the carbon atom in organic compounds, Meyer and Mark<sup>3</sup> have proposed a "primary valence chain model" of rubber, which conforms to the X-ray data and to the most important chemical properties. Since its general features have been pretty well confirmed, it seems a suitable time to improve this model, to develop it further structurally and to attempt to make clear the mechanical and other properties of the substance.

In the first step of this development, there is the problem of the position of the CH<sub>2</sub> groups at the double bond, *i. e.*, whether the CH<sub>2</sub> groups in the chain are in *cis* or in *trans* position to one another at the double bond.

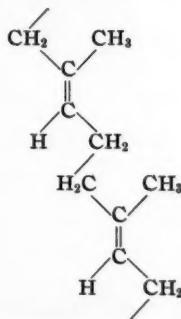
In *trans* position isoprene residues repeat themselves periodically (see Fig. 2), whereas in the *cis* position every other isoprene residue is turned at an angle of 180° to its neighboring one, and every two isoprene residues form a repeating period (see Fig. 1). The X-ray diagram favors the second (*cis*) orientation; the measured identity period of 8.1 Å.U. comprises two isoprene residues, and therefore indicates that the methylene groups are in *cis* position to one another.

Because of the "free mobilities," which in Fig. 1 are the three simple bonds of the carbon chain and designated 1, 2, and 3, there are theoretically four possible ways of joining the isoprene residues, as is shown in Fig. 1, Fig. 3a, Fig. 3b, and Fig. 3c.

The arrangement in Fig. 1 leads to straight chains, as X-ray diagrams indicate exist in stretched rubber. By a turning of the second isoprene residue around the freely moving bonds 1 and 2, or 3, the orientations shown in Figs. 3a, 3b, and 3c are obtained. It is obvious that the orientation in Fig. 3b is impossible for steric reasons, while the orientations in Figs. 3a and 3c are identical in principle, and by turning it will be discovered



*cis*-arrangement  
Figure 1



*trans*-arrangement  
Figure 2

that only the methyl groups and the hydrogen atoms at the double bond exchange places. Accordingly the four possibilities are reduced essentially to two, *viz.*, the straight form in Fig. 1 and the twisted form in Fig. 3a.

If more isoprene residues are added on, according to the same principle of bonding, a spiral is obtained, which according to the direction of its coiling may turn left or right (see Fig. 4).

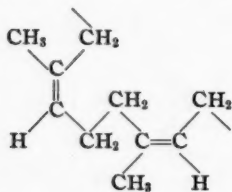


Figure 3a

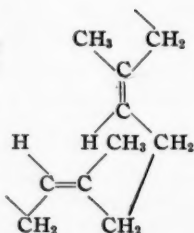


Figure 3b

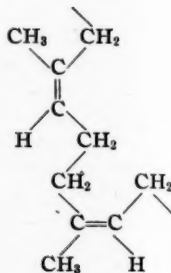


Figure 3c

The next problem is to show that unstretched rubber has the spiral form (see Fig. 4), that when stretched it assumes the extended chain form (see Fig. 1) and that this spiral model<sup>4</sup> agrees with the best known physical and chemical properties of rubber.

1. *Elasticity.*—The most striking property of rubber is its tremendously high "disproportionate" elasticity. Every model must therefore first of all explain the eightfold reversible elongation of rubber. To ascertain whether the model

described in the present paper does so, it was constructed mechanically out of spheres (see Figs. 5, 6, and 7). The large dark balls represent the carbon atoms, the small balls the hydrogen atoms at the double bond, and the light colored balls the methyl groups. The hydrogen atoms of the methylene and methyl groups were omitted for the sake of clearness. For the same reason, all bonds were made rigid, except the simple C-C bonds shown in Fig. 1 as I. The isoprene residues were held to these movable bonds by steel springs in such a way that there are not disrupted when the model assumes the spiral form

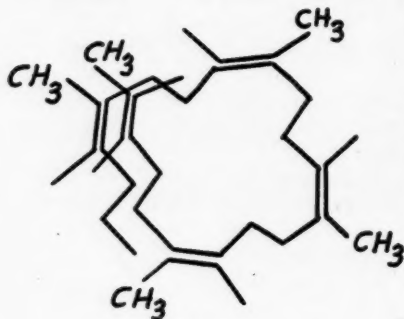


Figure 4

(see Fig. 5). The spiral form passes through the opening of one spiral after another (see Fig. 6) into the elongated chain. The spiral form passes through the opening of one spiral form (see Fig. 7, or diagrammatically Fig. 1).

The changes in length found in this model are about sixfold, and correspond to the reversible elongation of rubber. This model offers therefore a plausible explanation of the elongation of rubber. The visible elasticity of this substance is attributable to the primary valence chains.

Meyer<sup>6</sup> has recently developed a detailed theory of muscular contraction, based on the behavior of rubber, which agrees extremely well with known facts and which therefore supports in turn the considerations outlined below.

The effective force which causes the extended chains to coil again into spirals

when the stress is released is in the residual valences of the double bonds. If a stretched rubber crystallite is cooled to about  $0^{\circ}\text{C}$ ., it remains stretched even after the stress is released. If the temperature is now raised, the vibrations of the atoms become stronger and the rigidity of the structure is disrupted. Since internal van der Waals forces parallel to the direction of stretching are active, first one chain and then another moves sufficiently far out of range of the forces of attraction of adjacent chains and then contracts under the influence of their internal cohesive forces, *i. e.*, on warming the rubber relaxes and loses its crystalline structure. If the tension is retained at ordinary temperature, the chains are prevented from drawing together, and they keep their position in the crystallite. If the rubber is warmed, then at normal temperature the stress is no longer sufficient to prevent the twisting of the macromolecules and the crystalline structure and stress disappears. The heat tone accompanying the stretching and release agrees with these points of view, as may be seen in the following (Section 3).

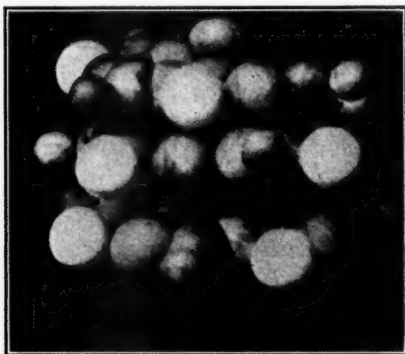


Figure 5

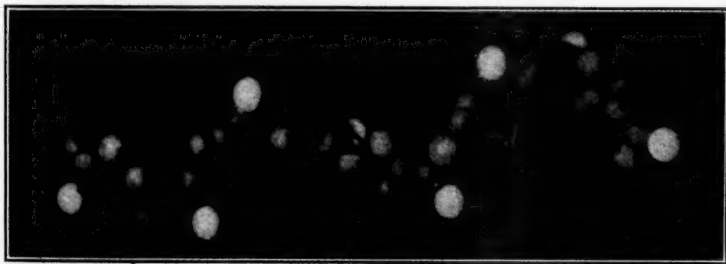


Figure 6

2. *The Work of Stretching.*—To overcome these internal van der Waals forces a certain amount of work must be expended during the stretching, and this work constitutes the reversible part of the work of stretching. The S-form of the elongation curve found experimentally can be explained in its relation to the active force in the following way.

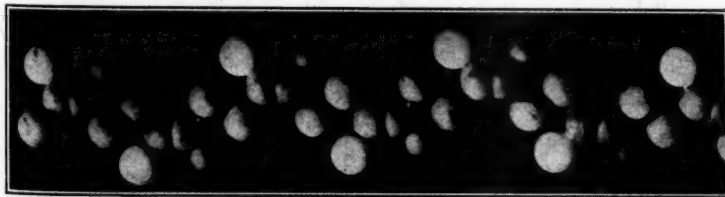


Figure 7

In the first part of the curve, up to about 80 per cent. elongation, a great force is necessary to open the spirals against the van der Waals forces (see Fig. 5), because the double bonds lie very close to one another. The curve begins therefore with a steep ascent. As a result a slight cooling takes place in this region, there are no X-ray interferences and only a very feeble optical and mechanical anisotropy. The force increases in proportion to the elongation, while one spiral after another is elongated into the extended chain. This phenomenon of "crystallization" can be followed quantitatively by the intensity of the X-ray interferences and by double refraction. It occurs with a positive heat tone. The final again rapidly ascending branch of the curve corresponds to the large work of elongation of the crystallites already formed.

With increasing temperature the heat motion of the atoms assists the loosening of the residual valences and diminishes the elastic work of elongation and the curves have a flatter course. The total work of elongation is greater on stretching slowly than on stretching rapidly on account of the flowing together of the chains (see Section 6).

3. *Heat Tone during Stretching and Release.*—On stretching, the rubber becomes warm above the first steep part of the elongation curve, and on release there is a corresponding cooling. The warming effect is only in small part an equivalent of the work expended in stretching, and for the greater part must be regarded as heat of crystallization, as suggested by Hock.<sup>6</sup> In fact the stretched rubber chains form a tightly constructed crystal lattice, the density of which is greater than that of the unstretched rubber. The crystallized phase, is, without tension, stable only when the stretched rubber is cooled below its "melting point," *i. e.*, when the heat vibrations are diminished so that the chains remain packed together. If the rubber is held under tension at higher temperature, the stretched rubber chains separate, disrupt the crystal lattice because of their heat vibrations, assume the spiral form, and lose their definite orientation. As a result the X-ray interferences disappear (finally completely) at the higher temperatures, the tension falls to zero and the rubber retains its elongation.

The "crystallized" state of rubber is therefore not under tension at lower temperatures, while at higher temperatures this state is stable only under a definite stress.

The heat tone on stretching is made up of three components:

(a) A negative heat tone to overcome the forces of attraction of the residual valences of the double bonds, which is large at the beginning of elongation and overbalances in this initial stretching (up to about 80% elongation) both the following components;

(b) An irreversible heat of friction, which appears as the equivalent of the plastic work of elongation;

(c) A heat of crystallization, which is set free when the elongated chains are arranged in the ordered crystal lattice. In conjunction with the heat of friction, this heat of crystallization is responsible for the strong positive heat tone during stretching and the cooling effect upon release of the rubber.

4. *Specific Volumes.*—A diminished specific volume accompanies the more compact and more orderly arranged lattice structure of stretched rubber.

5. *X-ray Interferences and Double Refraction.*—The crystal lattice of the extended primary valence chains in stretched rubber show the well-known X-ray interferences. The intensity of the interference points increases proportional to the elongation and to the degree of orientation,<sup>7</sup> and the intensity increases more slowly when the rubber is stretched slowly than when it is stretched rapidly. This is a result of a gradual slipping of the chains past one another (see Section 6). Double refraction runs parallel with the X-ray interferences.<sup>8</sup>

6. *Permanent Elongation.*—If unvulcanized rubber is stretched slowly while warm, it can be stretched to twenty or more times its original length. On release it does not fully recover to its original length, but at the most to an eighth of the maximum elongation. The increasingly irreversible or permanent elongation which accompanies an increasing period of elongation depends upon a slipping past one another of the chains. This slipping is the cause of the interdependence of work of elongation, heat of elongation, and intensity of interferences, and of these in turn with the rate of elongation.<sup>9</sup>

7. *Swelling and Solvation.*—The molecules of the swelling agent or solvent penetrate among the coiled spirals of rubber, saturate the residual valences of the double bonds and as a result cause in the medium a stretching of the primary valence chains during swelling and solution. If a thin film is prepared on a glass plate by evaporating a rubber solution, the chains adhere firmly together in the stretched form on the base. When the film is removed, the film immediately curls up, obviously because the chains revert to the spiral form, which is the stable form in the dry state.

8. *Vulcanization.*—Vulcanization brings about a union of the rubber chains through sulfur bridges. In soft rubber there are only a few sulfur bridges and the structure is retained in its essential form. It still shows therefore the elasticity and the reversible elongation of the raw rubber. Only the slipping of the chains past one another is inhibited by the sulfur bridges. Accordingly only swelling instead of complete solution takes place. In hard rubber the numerous sulfur bridges form a more intricate network of rubber chains, with increased rigidity and diminished elasticity.

9. By saturation of the double bonds with halogen or a hydrogen halide, the active force which coils the chains is removed, as shown particularly well in the experiments of Staudinger, and the products lose progressively their elastic properties as the degree of saturation increases, and when complete saturation is reached they become inelastic.

10. A quantitative hydrogenation of the double bonds of the rubber cannot be accomplished,<sup>10</sup> probably because of partial saturation of the double bonds among themselves or by the solvent. On the contrary, cyclicization takes place with extraordinary ease, *i. e.*, the double bonds superposed upon one another in the spirals are saturated mutually with ease, with formation of true C-C bonds. Such cyclicization takes place partially in the normal bromination of rubber, which is indicated by the separation of HBr and the substantially lower viscosity of the brominated products.

There are other properties of rubber which agree with the model described in this paper. For example there is the high resistance to tearing in the direction of the chains and the smaller resistance at right angles to this direction. Then the difference between sol- and gel-rubber can be explained on the assumption that ether, as a bad solvent of rubber, can dissolve out only the individual free rubber chains, while the chains which are more entangled remain behind as a swollen but intact structural form. In a good solvent like benzene there is no differences in the solubility and solvation of the two forms, because the solvent action is sufficient to tear apart the chains of gel-rubber from one another and dissolve them, so that all essential differences between the two forms of rubber become insignificant.

The foregoing arguments are not in any way a final settlement of the problem of the remarkable properties of rubber, but are only a step in that direction. The next step must be to show in a quantitative way with such a model the tensile strength and elongation curve of rubber with its accompanying phenomena, such as heat tone and appearance of interferences. The experimental data necessary



to correlate such an experiment with observed facts are however lacking, for up to the present time the elastic, thermal, X-ray, and chemical properties have never been studied with the very same material.

Accordingly the authors are now occupied in remedying this present lack of experimental data, and the model described in the present paper will be tested in a quantitative way with the aid of the new experimental results, and in this way will, if necessary, be modified or improved.

### References

- <sup>1</sup> This spiral model was described by Hauser at the 76th meeting of the American Chemical Society (cf. *Ind. Eng. Chem.*, **21**, 249 (1929)) and was also reproduced in a somewhat misunderstood form by F. H. Cotton (cf. *India Rubber J.*, **1929**, 46). The figurative representations 6 and 7 do not correspond to the conceptions of the original authors.
- <sup>2</sup> Mark and Susich, *Kolloid-Z.*, **46**, 11 (1928).
- <sup>3</sup> Meyer and Mark, *Ber.*, **61**, 1939 (1928).
- <sup>4</sup> Spiral models of rubber have already been repeatedly proposed. A spiral feather model of the rubber molecule was proposed by Barrow and was used by Wechsler to explain the chemical behavior of rubber (cf. Ditmar, *Der Kautschuk*, **1912**, p. 47). There is also the model of Feuchter. The model proposed in the present paper attempts to emphasize more precisely the details of structure than do the previous models.
- <sup>5</sup> Meyer, *Biochem. Z.*, **214**, 17 (1929).
- <sup>6</sup> Hock, *Kolloid-Z.*, **35**, 40 (1925).
- <sup>7</sup> Katz, *Chem.-Zig.*, **49**, 353 (1925); *Naturwissenschaften*, **13**, 411 (1925); Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63; **23**, 64 (1926).
- <sup>8</sup> Zocher, *Kautschuk*, **5**, No. 8 (1929).
- <sup>9</sup> Hauser and Rosbaud, *Kautschuk*, **4**, 12 (1928).
- <sup>10</sup> See the important works of Staudinger and of Pummerer.

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In an article with the same title in *Kautschuk*, pages 31-33, February, 1930, Kirchhof discusses earlier investigations of his own, which led him to develop a spiral model himself at the time.

A review of this article of Kirchhof by Fikentscher and Mark led these last two authors to make the following remarks concerning the ideas and model of Kirchhof.

"Kirchhof has had the kindness to send us the manuscript of his paper. Unfortunately his earlier work was overlooked in our survey of the literature. It shows us that eight years ago Kirchhof had visualized all the essential features of the spiral model, and we believe that the increased knowledge of the present day of the physical, mechanical, and chemical properties of rubber shows that such a model is a good representation of the facts."

This earlier work of Kirchhof may be found in the following sources: *Kolloid-Z.*, **30**, 176 (1922); *Kolloidchem. Beihefte*, **16**, 47 (1922).

# The Influence of the Principal Accelerators of Vulcanization on the Preservation of Rubber

R. Thiollot and G. Martin

In the April and October, 1929, issues of *le Caoutchouc & la Gutta-Percha* the authors have shown that accelerators of vulcanization can be classified according to: (1) their precocity, (2) their temperature of normal action (characteristic temperature), and (3) their rapidity of action at the characteristic temperature.

The "plateau of vulcanization" was studied for each accelerator. In order to complete the work it has been necessary to study the influence of the principal accelerators of vulcanization on the preservation of rubber. This article gives the result of these experiments.

Mixtures of "pure gum" type were prepared, containing the principal accelerators of vulcanization, taking as a basis the following mixture:

Pale crepe	100
ZnO	5
Palm oil	1
Stearic acid	0.5
Accelerator	...
S	...

The proportions of accelerator and of sulfur used are given in the accompanying table. They correspond to those employed in practice.

No.	Name of the Accelerator	Proportion of Sulfur to Rubber	Proportion of Accelerator to Rubber
1	Zn isopropylxanthate	2	2
2	Zn methylphenyldithiocarbamate	1.8	0.7
3	Tetramethylthiuramdisulfide	1.8	0.4
4	Mercaptobenzothiazole	2.5	0.7
5	Diphenylguanidine	3	0.7
6	Di- <i>o</i> -tolylguanidine	3	0.6
7	Phenyltolylxylylguanidine	3	0.6
8	Ethylideneaniline	3.5	1
9	<i>p</i> -Nitrosodimethylaniline	3.5	1
10	Thiocarbanilide	5	2.5
11	Anhydroformaldehyde- <i>p</i> -toluidine	3.5	1
12	Anhydroformaldehydeaniline	4	2
13	Triphenylguanidine	3.5	1

**Choice of Conditions of Vulcanization.**—Each of the mixtures was vulcanized under pressure. The characteristic temperature of the accelerator was used as the temperature of vulcanization. Two times of vulcanization were then selected. If "*t*" is the time required to give the maxima mechanical properties to the mixture the first length of time *T* will be determined by

$$T = t - \frac{t}{5}.$$

It corresponds, therefore, to a slight undercure vulcanization. It is the cure used in industrial practice.

For the second time of vulcanization  $T'$ , the time is chosen at which the mechanical properties of the vulcanized mixture commence to deteriorate. These two times  $T$  and  $T'$  are determined by an examination of the graphs published in *le Caoutchouc & la Gutta-Percha*, October, 1929.

*Example.*—The mixture containing di-*o*-tolylguanidine vulcanized at 3 kg. (characteristic temperature) presents optima mechanical properties at a cure of 70 min. Vulcanization for more than 110 min. causes deterioration. We have therefore selected as conditions for vulcanization

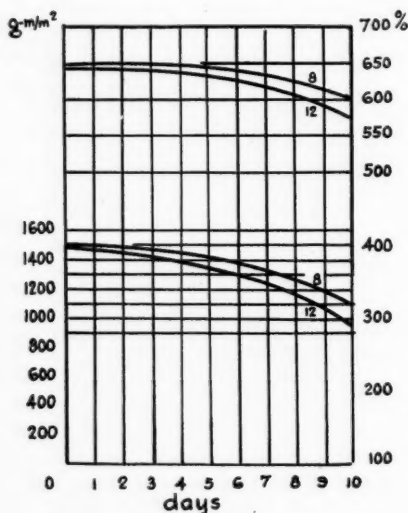
(1) temperature

3 kg.

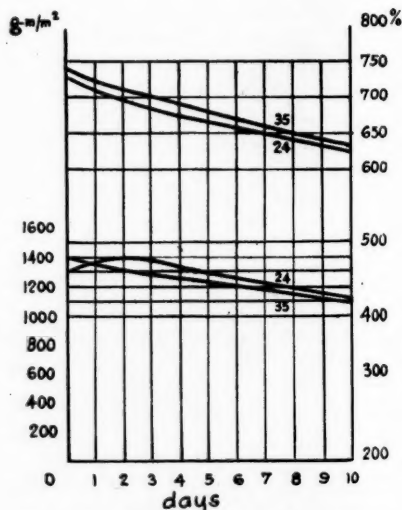
$$\text{time } T = 70 - \frac{70}{5} = 56 \text{ min.}$$

(2) temperature

time  $T' = 110 \text{ min.}$



Graph I—Zinc Isopropylxanthate

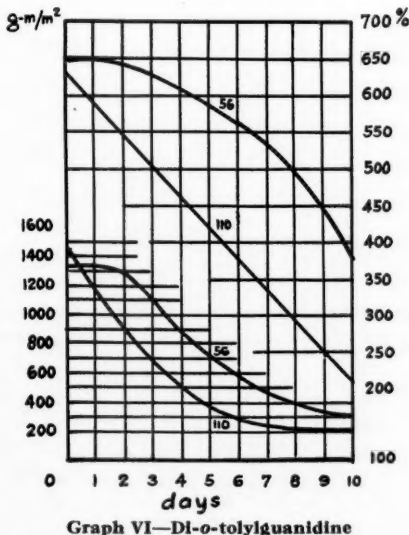
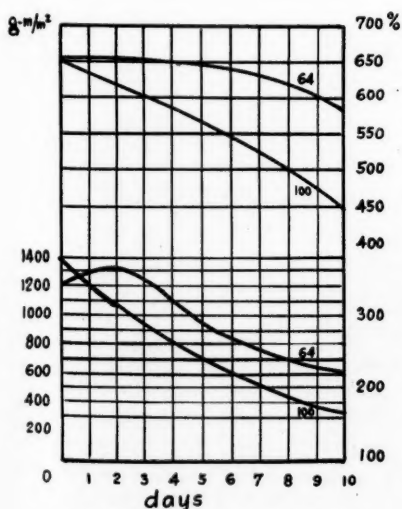
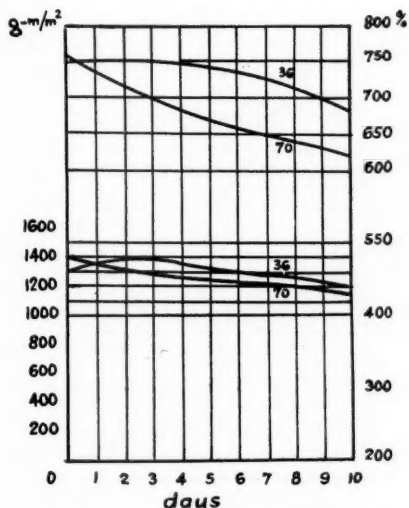
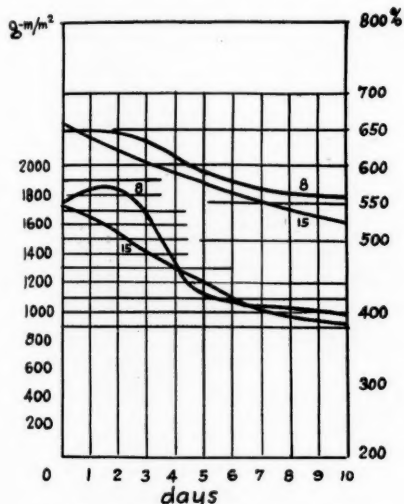


Graph II—Zinc Methylphenyldithiocarbamate

The following table summarizes the conditions under which the experiments were carried out.

Name of Accelerator	Steam Pressure at the Charac- teristic Temperature	$t$	$T$	$T'$
Zn methylphenyldithiocarbamate	1 kg.	30	24	35
Tetramethylthiuramdisulfide	2	10	8	15
Mercaptobenzothiazole	3	45	36	70
Diphenylguanidine	3	75	64	100
Di- <i>o</i> -tolylguanidine	3	70	56	110
Phenyltolylxylylguanidine	3	80	64	100
Ethylideneaniline	2.5	50	40	80
<i>p</i> -Nitrosodimethylaniline	2.5	75	60	95
Thiocarbamilide	3	110	88	130
Anhydroformaldehyde- <i>p</i> -toluidine	3	75	60	90
Anhydroformaldehydeaniline	3	90	72	100
Triphenylguanidine	3	85	68	110
Zn isopropylxanthate	100° C.		8	12

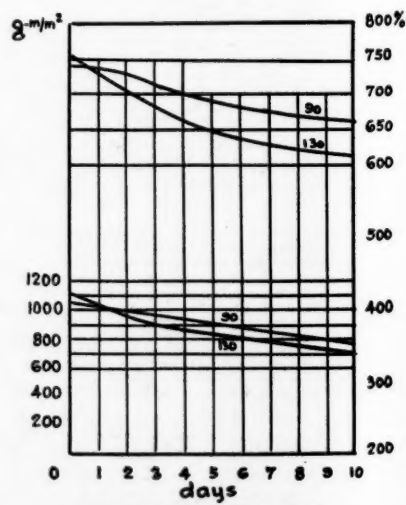
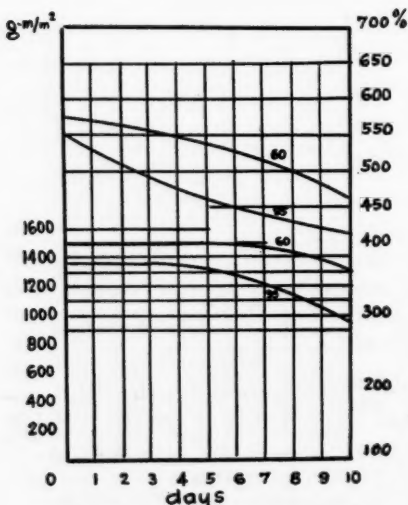
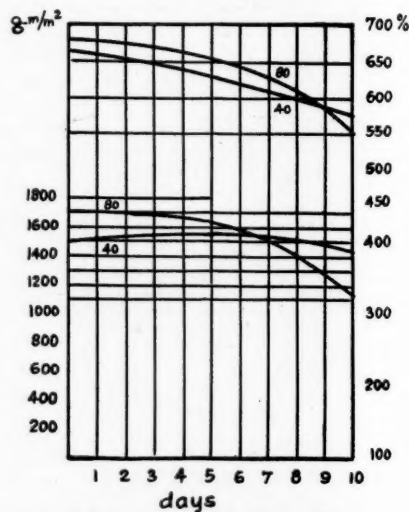
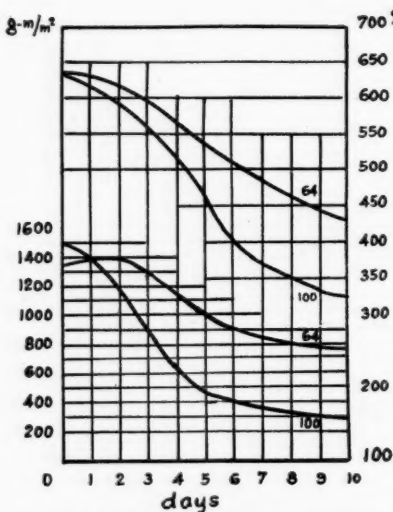
For Zn isopropylxanthate, an example of a very active class of accelerators serving special uses, *i. e.*, self-curing solutions, cures were carried out at 100° C., though this temperature cannot be considered the characteristic temperature of this accelerator.



**Aging Tests.**—Test rings of carefully determined dimensions were cut from each vulcanized mixture. The test pieces were then placed in a ventilated oven heated by an electric resistance where a control served to keep the temperature constant at 70° C. Every other day three samples of each mixture were taken. After

24 hours' rest strength tests were made. Each figure represents the value of three experiments. The total duration of test was 10 days.

*Representative Curves.*—With the abscissae representing the times of heating and the ordinates the tensile strengths, curves were drawn representing the way in



which tensile strength varies with increase in time of heating. Similar curves were drawn to represent the per cent. of elongation to rupture.

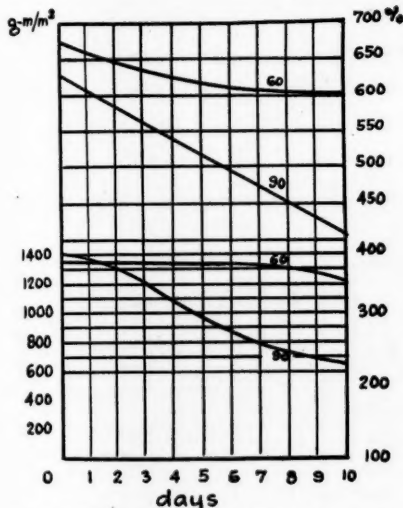
In all the graphs shown hereafter the time of heating in days is shown on the x axis.



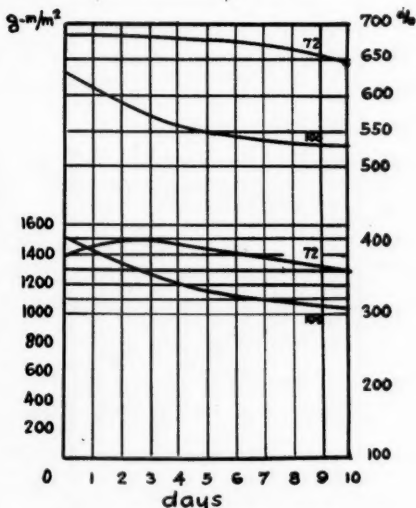
The two curves located nearest to the  $x$  axis correspond to the tensile strength in g. per sq. mm. indicated on the  $y$  axis at the left. The two curves located farthest from the  $x$  axis correspond to the per cent. elongations at rupture shown on the  $y$  axis at the right. The number of each curve indicates the time of cure in minutes at the characteristic temperature.

**Results.**—An examination of the curves shows that mercaptobenzothiazole and the condensation products of aldehyde amines—ethylideneaniline, anhydroformaldehydeaniline, and anhydroformaldehyde-*p*-toluidine—give to mixtures of the pure gum type remarkably good aging properties.

Taking into consideration the results learned previously it can be stated that mercaptobenzothiazole and ethylideneaniline present a group of characteristics that make them accelerators of great interest: medium precocity, sufficiently great activity, long plateau of vulcanization, good aging. Mixtures vulcanized with



Graph XI—Anhydroformaldehyde-*p*-toluidine



Graph XII—Anhydroformaldehydeaniline

these two products even for a time of cure corresponding to a very marked over-vulcanization age in a very satisfactory manner.

This group of properties makes mercaptobenzothiazole and ethylideneaniline useful in the manufacture of a large number of articles, the former in the composition of light mixtures, the latter in dark or black mixtures.

In the class of rapid accelerators, Zn methylphenylthiocarbamate gives to mixtures aging properties which are remarkable for accelerators of this type. On the contrary, the group of guanidines—diphenylguanidines, di-*o*-tolylguanidines, triphenylguanidine, phenyltolylxylylguanidine—do not give good aging properties to mixtures. After 240 hours in an aerated oven, at a temperature of 70° C., the mechanical properties of mixtures vulcanized with these products lose 50 to 80% of their quality.

It is necessary, in order to vulcanize with these compounds, to use an antioxidant to improve the aging of the manufactured articles. It should be observed that the bad aging of mixtures accelerated with guanidines is noticeably less marked for loaded mixtures than for pure gum mixtures.

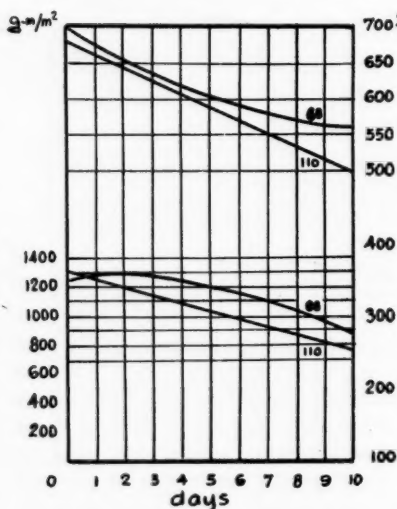
### Effect of Simultaneous Use of Two Accelerators

Some examples of the simultaneous use of two accelerators mentioned in the following table were studied:

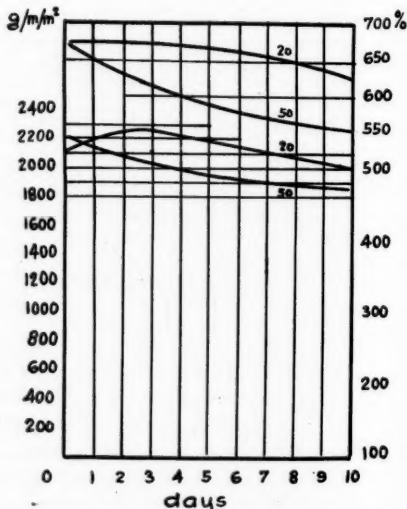
Name of Accelerator	Ratio of Sulfur to Rubber	Ratio of Accelerator to Rubber
Mercaptobenzothiazole	2.5	0.3
Ethylideneaniline		0.45
Mercaptobenzothiazole	2.5	0.3
Diphenylguanidine		0.4
Zn methylphenyldithiocarbamate		0.7
Anhydroformaldehydeaniline	1	1

The times of vulcanization  $T$  and  $T'$  were chosen on the same basis as for mixtures containing only one accelerator. The accompanying table gives the conditions under which the tests were carried out.

Name of Accelerator	Steam Pressure at Characteristic Temperature	$t$	$T$	$T'$
Mercaptobenzothiazole	2 kg.	25	20	50
Ethylideneaniline				
Mercaptobenzothiazole	1.5	40	32	60
Diphenylguanidine				
Zn methylphenyldithiocarbamate	1	30	24	40
Anhydroformaldehydeaniline				



Graph XIII—Triphenylguanidine



Graph XIV—Mercaptobenzothiazole and Ethylideneaniline

It has already been shown that combinations of mercaptobenzothiazole with diphenylguanidine and ethylideneaniline behave like rapid accelerators with long plateaux of vulcanization. An examination of our graphs will show that these combinations also give good aging properties to the mixtures.

It has been shown that anhydroformaldehyde aniline makes rapid accelerators easier to handle by decreasing the tendency to scorch mixtures on the rolls and in

the tube machine or to cure prematurely. This study shows that anhydroformaldehydeaniline also gives equally good aging properties to mixtures vulcanized with this type of accelerator.

*Example.*—The mechanical properties of a mixture containing 0.7% Zn methylthiocarbamate and 1.8% sulfur, cured 24 min. at 1 kg., lose 27% of their value on heating in the oven 240 hours. If 1% anhydroformaldehydeaniline is added, the mechanical properties lose only 15% in the same heating.

These results are sufficient to show that one should always consider the use of anhydroformaldehydeaniline in the manufacture of mixtures vulcanized with rapid accelerators

*Interpretation of the Results.*—Designating by  $A$  the per cent. elongation at rupture and  $C$  the stress at rupture in g. per sq. mm. for a given mixture, the product  $A \times C$  gives an indication of the mechanical value of the mixture.

The results of these experiments can thus be interpreted by comparing for a single mixture the products  $A \times C$  before heating and after heating in the oven. The greater the diminution of this product as a result of heating, the poorer is the aging. The results of these determinations are given in the following table, where, in order to simplify the figures, the products  $A \times C$  have been divided by 10,000.

Name of Accelerator	Time of Vulcanization	Temperature of Vulcanization	$A \times C$ 10,000 before Heating	$A \times C$ 10,000 after Heating	% Loss of Product $A \times C$
Zn methylthiocarbamate	24 m.	1 kg.	94.5	68	27%
	35		103	68	34
Tetramethylthiuramdisulfide	8	2	114	56	51
	15		115	50	56.5
Mercaptobenzothiazole	36	3	98	82.5	13.5
	70		106	73	31
Diphenylguanidine	64	3	78.5	37	51
	100		90	16	82.5
Di- <i>o</i> -tolylguanidine	56	3	88	12.5	86
	110		91	4	96
Phenyltolylxylylguanidine	64	3	86	32.2	62
	100		95	10	90
Ethylideneaniline	40	2.5	100	83.5	16.5
	80		116	74.5	36
<i>p</i> -Nitrosodimethylaniline	60	2.5	86.5	63	27
	95		76	40	47.5
Thiocarbanilide	90	3	68	40.5	40.5
	130		72	34	53
Anhydroformaldehyde- <i>p</i> -toluidine	60	3	91	74	18.5
	90		88	28	68
Anhydroformaldehydeaniline	72	3	98	83.5	15
	100		95	55	42
Triphenylguanidine	68	3	86.5	50	42
	110		86.5	38.5	56.5
Mercaptobenzothiazole and ethylideneaniline	20	2	142	125	12
	50		142.5	103	27.5
Mercaptobenzothiazole and diphenylguanidine	32	1.5	125	106	15
	60		146	98	33
Zn methylphenyldithiocarbamate	24	1	123.5	102.5	17
and anhydroformaldehydeaniline	40		124	102	19.5
Zn isopropylxanthate	8	100° C.	97.5	66	32
	12		96	54.5	43

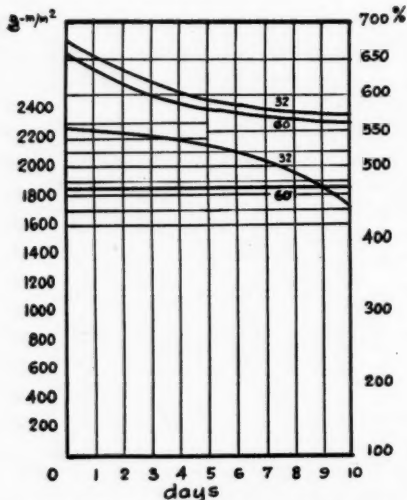
According to their influence on the aging of a pure gum mixture, the accelerators of vulcanization studied can be grouped as follows:

- (1) Loss of product  $A \times C$  from 0 to 20%: Zn methylphenyldithiocarbamate

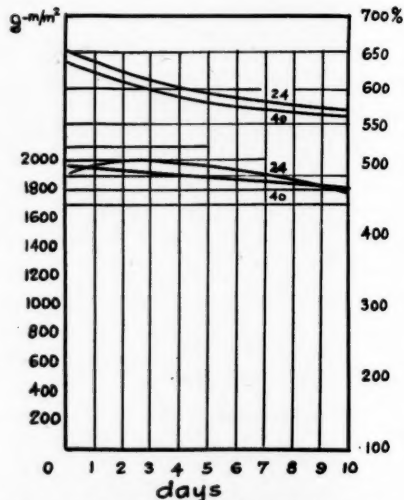
and anhydroformaldehydeaniline; mercaptobenzothiazole; ethylideneaniline; anhydroformaldehydeaniline; anhydroformaldehyde-*p*-toluidine; mercaptobenzothiazole and ethylideneaniline; mercaptobenzothiazole and diphenylguanidine.

(2) Loss of product  $A \times C$  from 20 to 40%: Zn isopropylxanthate; Zn methylphenyldithiocarbamate; *p*-nitrosodimethylaniline; thiocarbanilide.

(3) Loss of product  $A \times C$  above 40%: tetramethylthiuramdisulfide; diphenylguanidine; di-*o*-tolylguanidine; phenyltolylxylguanidine; triphenylguanidine.



Graph XV—Mercaptobenzothiazole and Diphenylguanidine



Graph XVI—Zn Methylphenyldithiocarbamate and Anhydroformaldehydeaniline

# The Surface Energy between Rubber and Fillers

Fritz Hartner<sup>1</sup>

The purpose of this research was to increase the reliability and accuracy of the calorimetric method elaborated by Bostroem,<sup>2</sup> and to discover and overcome any difficulties or sources of error in order that the method might be applicable to the investigation of problems concerning the chemistry and technology of rubber.

The following points were to be considered:

1. The dependence of the "reinforcing" action of a filler on its concentration, and the utilization of the surface energy between rubber and filler.
2. The evaluation of the surface tension in the system raw rubber/filler.
3. The aging phenomenon of rubber and the possibility of making it reversible.
4. The comparison of various commercial gas blacks at a given concentration.

## Procedure in Using the Calorimeter

A differential calorimeter was employed similar to that described by Bostroem.<sup>3</sup> The galvanometer used by Bostroem was replaced by a small Siemens and Halske instrument, whose sensitivity was about  $10^{-4}$  amperes. The iron-constantan thermoelement with 36 couples was found to be exceptionally fragile and was replaced by a new one of copper-constantan with about 100 couples. It was possible to increase the sensitivity of the apparatus so that 1 mm. on the scale of the galvanometer mirror corresponded to a temperature difference of about  $2 \times 10^{-4}^{\circ}\text{C}$ . in the Aurophan beakers. Hence minute effects could be measured with a reproducible accuracy of 5-7%.<sup>4</sup>

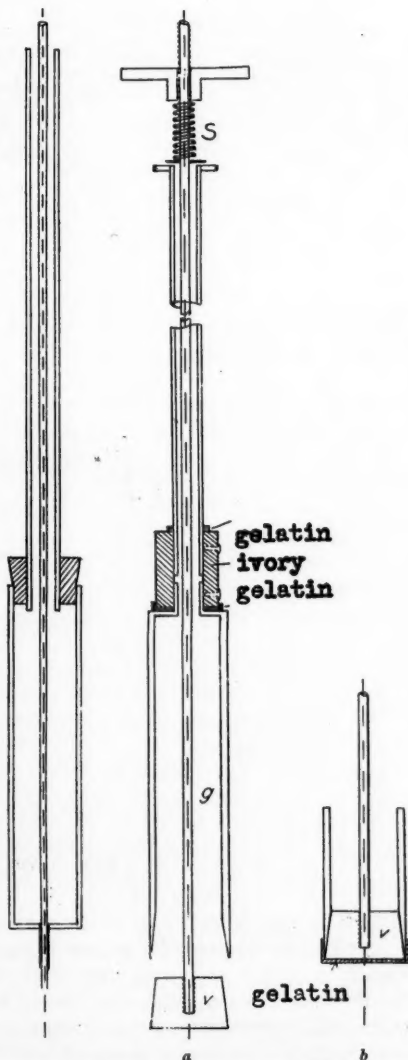


Figure 1—Reaction Chamber, Old Form Figure 2—Reaction Chamber, New Form



The brass shells used by Bostroem to hold the reacting materials had two important disadvantages. They were closed by a long wire cemented in place with water-glass. This wire was removed at the beginning of the reaction, thereby giving free vent to an opening 1.5 mm. in diameter (Fig. 1). Thus it often happened that the closure was not sufficiently tight, and when an attempt was made to overcome this difficulty by using very thick water-glass and allowing it to dry longer, the wire became so firmly fastened that it was impossible to withdraw it at an

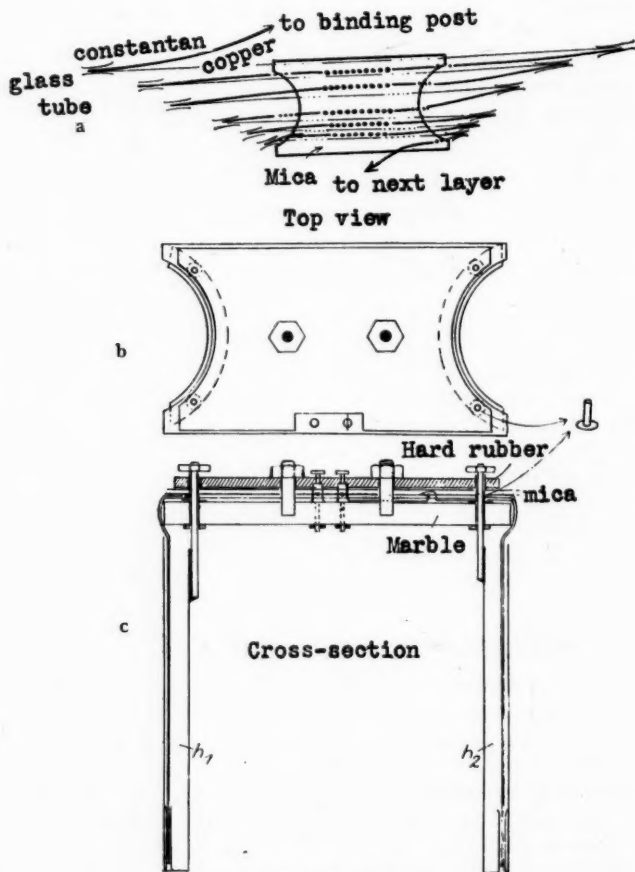


Figure 3—The Thermoelement

accurately determined moment. A trial run showed that the frictional heat developed under these conditions was not to be disregarded in measuring small effects. Finally it took a very long time to fill the shells through the small opening with the swelling medium, and also the opening easily became plugged up, especially when using powdery materials, before the vessels were completely full. Therefore new reaction vessels were provided with broad metallic edges below, which proved excellent (Fig. 2). The brass vent  $v$  at the bottom was closed by means of a 50% gelatin solution. After filling the vessel  $g$  and turning the screw  $s$  down slightly,

the hot gelatin solution was drawn up by means of a pipette with a wide opening so that on cooling a ring was formed as shown in Fig. 2b. After 10 or 15 minutes (only in very damp weather was a longer time required), it was possible to set the vessels in the calorimeter and begin an experiment. When the course of the calorimeter had become constant, the screw was loosened and at the desired moment the vessels were opened by a slight tap with a little lead hammer on the upper end of the valve spindle.

The construction of the new thermoelement is shown in Fig. 3. Double silk-covered copper and constantan wires were drawn alternately through a number of layers of mica. The wires of the first layer were as long as the reaction vessels were deep; those of the last layer ended close to the surface of the swelling medium. Five such layers were soldered together, placed on the pegs in the marble plate of the element, covered with a sheet of hard rubber, and held in place by the female screws in the middle (Fig. 3b). Long thin glass tubes, open at both ends, were drawn over the individual couples. The group of couples on either side projected into the semi-circular shells  $h_1$  and  $h_2$  (Fig. 3c). Since naphtha was used as the swelling fluid, the heat transfer was simply obtained by boring a few small holes in the brass shells. When fluids which were good conductors were used, the shells, instead of being bored, could be treated on the inside with paraffin and lead shot so as to obtain a thermal contact on the inside.

The first copper wire of the first layer and the last constantan wire of the uppermost layer were connected to the two clamps. Thence two thick wires led across a unipolar circuit-breaker to the galvanometer, which stood on a ground glass plate.

The reading glass and scale were mounted on a solid pillar.

Despite these precautions it seemed almost impossible to work during the day time as the least jar such as caused by someone passing in the corridor or a truck going along the street or especially the operation of an oil pump threw the galvanometer into vibration.

Mention may be made of a very disturbing phenomenon, which often occurred, and which it took a long time to overcome.

Occasionally the galvanometer twitched a few millimeters one way or the other at each cycle of the stirring mechanism, so that positive readings were hardly possible. At first it was thought that the stirrer in the Aurophan beakers was grazing or touching some poorly insulated wire, but this proved to be not the case. Likewise it was not a question of vibrations being transferred to the instrument. The observation that the phenomenon occurred particularly in damp weather and disappeared of its own accord with better weather led to its circumvention.

The driving motor was operated from the 70-volt line in series with a considerable resistance. The conductivity of the film of moisture which formed in damp weather on the motor, the belt, and the glass plate on which the galvanometer stood was sufficient to ground through the instrument a fraction of the motor's current. As the resistance of this shunt circuit varied with the depth of the position of the glass stirrer, the galvanometer necessarily vibrated in time with the stirring mechanism.

It was an easy matter to calculate that the phenomenon should occur as soon as the resistance of the connection between the stirring motor and the galvanometer (*i. e.*, the leather belt and the liquid in the Aurophan beakers) fell below  $3.5 \times 10^4$  megohms, which, naturally, happened very easily in damp weather.

Replacing the leather belt by a rubber tube with the ends cemented together was not a success, as the latter proved to be too elastic, so that the stirrer did not move at a uniform rate, speeding up on the down stroke because of its weight on the motor, then holding back on the up stroke because of the depth of its position,

and speeding up again with a jerk at the end of the half turn of the pulley. The simplest remedy proved to be to keep on hand two belts that fitted, and to work with one while the other was being dried out to be used when needed.

Bostroem connected the heating coils used in calibrating the apparatus for each experiment to the thermoelement plate. This procedure was abandoned when the new apparatus was used, because the switching-in of the heating current in the old model sometimes produced disturbances in the galvanometer. Instead the coils were fastened to the stirrer, whereby the further advantage was obtained that the instrument reacted much more quickly than formerly to the switching-in of the heating current. The resistance of the heating coils in the reaction vessels was 5.78 ohms.

The procedure adopted was as follows: The rubber used was in the form of sheets 1-1.5 mm. thick and  $10 \times 12$  cm. along the sides. To obtain better heat transfer these sheets were milled on to a wire gauze. The weight of the rubber was accurately known.

One of these sheets was then rolled up with a piece of wire gauze in such a way that rubber did not touch rubber at any point, and at the same time the solvent (which was always the same, naphtha dried over calcium chloride) could penetrate everywhere quickly and surely. The whole roll was wrapped in a piece of thin parchment paper, for it was found that the reaction vessels, once they were smeared with swollen rubber, could be cleaned only with difficulty and much loss of time, without scratching and damaging the valve-seating at the bottom, thereby causing it to leak. The little package thus formed was introduced into the reaction chamber, the valve spindle stuck through, and the valve seated tightly, not by turning (for then it could hardly be loosened), but by striking it a light blow with a wooden hammer; the disc and spring above were then put in place and the screw turned down slightly. In the other chamber there was a similar piece of wire gauze and parchment paper. The two chambers were then sealed with gelatin as shown above (Fig. 2b). After drying the calorimeter, it was assembled and the stirring mechanism introduced. By heating one or the other coil, the position of the galvanometer could be suitably regulated according to the magnitude and sign of the effect expected. This was not a difficult matter, and the whole operation consumed about half an hour. Then observations of the process were begun, the reading period requiring two minutes. Constancy was reached in half an hour to an hour, depending on the difference between the converging temperatures. When the readings had become constant, the screws on the reaction chamber were loosened and at the desired moment (*i. e.*, simultaneous with a reading) the reaction was started by a slight tap with a small lead hammer on the projecting end of the valve-spindle. The duration of the principal part of the process thus started depended upon the substances to be swollen. If it was only a question of wetting a powder, then usually constancy again obtained in thirty to forty minutes; on the other hand if old or heavily loaded rubber was under examination, this part of the experiment could take up to two hours.

When constancy was again obtained, the current was turned on in the heating coils in the reaction chamber in order to calibrate the apparatus. The density and duration of the current were so regulated that the effect produced was of about the same magnitude as the swelling effect and also the same duration except in the case of excessively long periods.<sup>5</sup>

The amperage of the heating current was read at half minute intervals, and the average of the readings taken. A Schöller universal galvanometer was used, which permitted reading to  $10^{-3}$  amperes, and which was compared with a standard instrument.

After cutting out the heating current, constancy usually again obtained in about twenty minutes. Then six or eight more readings were made and the experiment ended.

The duration of an experiment from the preparation to the end consumed at least 2.5 hours, and occasionally more than four hours.

Since it was shown that the variations in evaluating the readings according to the graphic method as opposed to the exact method of Roth<sup>6</sup> lay within the experimental error, in order to save time the readings were plotted directly on coördinate paper. It proved convenient to put 1 cm. on the ordinate axis equal to four minutes, and 1 cm. on the abscissae equal to 1 cm. on the scale of the galvanometer mirror.

[A representative calculation is here given in detail by the author.]

Moreover, by a large number of preliminary experiments it was shown that heating the reaction chamber for varying periods of time and different current strengths gave results by the graphic method of calculation that were completely satisfactory within the limit of accuracy desired. For example, it made no difference whether the current was applied for about sixty seconds at 0.4 ampere or 960 seconds at only 0.1 ampere. In both cases the corrected galvanometer reading was the same.

#### The Filler Problem and the Surface Energy between Raw Rubber and Filler

It has long been known that the physical properties of rubber can be greatly improved by the admixture of so-called "reinforcing" materials. The most important of these materials are: (1) certain gas blacks; (2) zinc oxide; (3) basic magnesium carbonate; (4) clay; and a few other inorganic compounds. The work required to rupture a rubber compound containing such materials is considerably greater than when rubber alone is present. It has been found that the finer a given filler is, the greater is the "resilient energy" or work required to rupture.<sup>7</sup>

By a long and carefully planned series of experiments, Wiegand<sup>8</sup> has shown that the reinforcing action of a filler is primarily dependent on the surface it presents, that is, this action is a function of the surface energy of the rubber-filler interfaces. Wiegand was also the first consciously to express the reinforcing action in units of work. On coördinate paper he plotted the tensiles as the ordinates and the corresponding elongations as the abscissae, and by measuring with a planimeter the area between the curve and the abscissa, determined the work performed, which he then expressed in cc. of the original compound. The work required to rupture, Wiegand called "proof resilience."

Wiegand determined the effect of the concentration of a filler in a compound in the following way. In a base mix<sup>9</sup> whose resilient energy was to some extent independent of the time of cure, he incorporated various amounts of filler and determined the proof resilience in each case. Thus he obtained a curve which expressed this value with regard to the concentration of filler.<sup>10</sup>

As shown by Fig. 4 (which is for a zinc oxide mix), the proof resilience increases to a maximum with increasing concentration and then falls off. If the horizontal

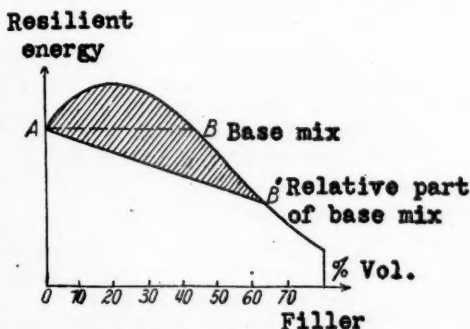


Figure 4—Effect of Addition of Filler on Resilient Energy of Rubber. (W. B. Wiegand)

line  $AB$  in the diagram represents the proof resilience of the base mix, then the area between it and the curve, which is a measure of the reinforcing effect of the filler, is called by Wiegand the "A function."

A study of the diagram indicates that after a definite concentration is reached, the filler no longer increases, but rather decreases the proof resilience. However, this is only apparently so, as in each case Wiegand based his calculations on the resilient energy of the base mix. If one takes for a line of comparison the resilient energy of the quantity of base mix present in any compound (*i. e.*, the line  $AB'$  in the diagram) this contradiction vanishes immediately. The point at which the oblique line  $AB'$  is crossed by the curve, or in other words the point at which the base mix is apparently weakened by the filler is where rubber is no longer being compounded with filler but filler is being compounded with rubber. Then the proof resilience of the filler, which itself is 0, is increased due to the presence of the rubber, usually attaining a positive value for the first time.

The latter part of Bostroem's work included a series of experiments which were intended to show the dependence of the reinforcing action of a filler upon its concentration. The following measurements were made: (1) the heat of swelling of raw rubber in naphtha; (2) the heat of wetting of the filler by naphtha; (3) the heat of swelling of the mixture in naphtha.

These three values permit the calculation of the reinforcing action in the following way: The heat of swelling of rubber was  $-0.1$  cal./g. rubber, the heat of wetting of the gas black was  $+2.8$  cal./g. black, and the heat of swelling of a mixture consisting of 8.5% by volume of 15% by weight of black was  $-0.35$  cal./g. compound. The following calculation could then be made:

1 g. compound contains 0.85 g. rubber and 0.15 g. black	
0.85 g. rubber on swelling gives	-0.085 cal.
0.15 g. black when wet gives	+0.420 cal.
1 g. compound therefore should give	+0.335 cal.
Instead there are obtained on swelling 1 g.	-0.35 cal.
Difference	-0.685 cal.

Therefore 0.68 cal. are consumed to overcome the bond between the rubber and the black. Since 1 g. of the compound contained 0.15 g. black, 1 g. black at a concentration of 8.5% by volume would require 4.53 cal. to overcome the force of adhesion. Calculated on the basis of 1 cc. of black we have

$$U_c = 7.96 \text{ cal./cc. (Sp. gr. gas black} = 1.75)^{11}$$

In every day practice the magnitude of the reinforcing action of a filler is determined with a Schopper machine in the following way:

Rings are died out of the rubber compound exactly 14 cm. inner circumference and 2 mm. thick, the cross section being about 4 mm<sup>2</sup>. These rings are placed in the Schopper tensile machine and slowly stretched to the breaking point.

The tensile machine is a dynamometer operating as an inclined pendulum which permits the reading in kg. of the force applied corresponding to any degree of elongation.

Attachments to the apparatus automatically draw curves during the stretching operation, which plot the elongation as the abscissae and the tensile as the ordinates. The apparatus used in this work was made by the Peters Union Co. in Frankfort, and was a simpler model, designed for testing textile fibres. The curves given in Fig. 5 were obtained by reading from the scale the tensile in grams at each elongation of 3 cm. The points obtained are given. The end of the curve indicates the moment of rupture of the test piece.

If it is desired to express the elongation at break in per cent., it must be remem-



bered that a ring of 14 cm. inner circumference has its circumference increased two-fold when the draw-bar has moved 7 cm.; that is, the test piece is elongated 100% at this point.<sup>12</sup> The area between the curve and the abscissa up to the point of rupture is manifestly a measure of the energy expended in breaking the test piece. The numerical value of this energy may be determined by means of a

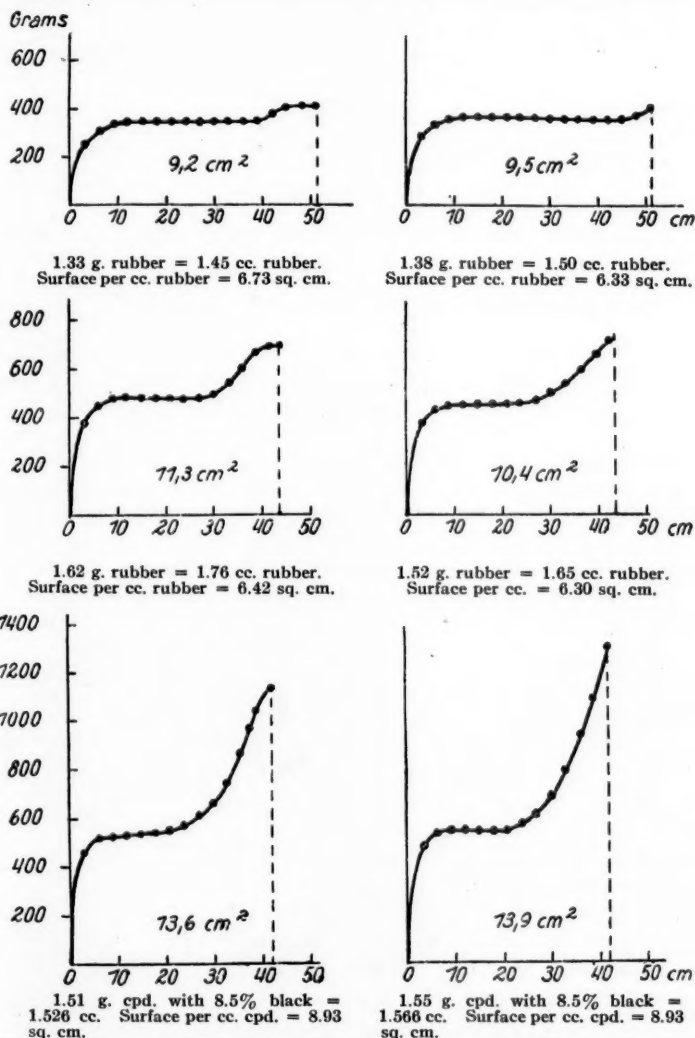


Figure 5—Tensile Curves. 1 Sq. Cm. = 0.02 Mkg. = 0.0468 Cal. (Ordinates = Tensile in G. Abscissae = Elongation in Cm.)

planimeter. The curves given are drawn so that 1 mm. on the ordinates corresponds to a movement of the draw-bar of 1 cm. On the abscissae, 1 cm. represents 200 g. tensile. Therefore 1 sq. cm. of the surface measured by the planimeter corresponds to 0.02 kilogram meters or 0.0468 gram-calorie.

In rubber technology it is customary to speak of units of volume. Hence, the stress-strain curves may also be calculated on the basis of calories per cc. (sp. gr. rubber = 0.92). The four stress-strain curves for raw rubber give as an average the following values:

One cc. of raw rubber gives 6.35 sq. cm. of surface as measured by the planimeter. Since 1 sq. cm. of this surface corresponds to 0.0468 calorie, the work of rupture of raw rubber may be calculated as 0.296 gram-calorie per cc.

Analogously we obtained from the curves for the gas black compound:

Work to rupture ( $= A'$ ) = 0.418 cal./cc.

The specific gravity of the gas black compound is 0.99, for

0.915 cc. rubber weighs	0.842 g.
0.085 cc. gas black weighs	0.149 g.
1.000 cc. compound (8.5% black by volume)	0.991 g.

These values permit the calculation of the reinforcing action as follows:

The value for the compound is	0.418 cal./cc.
In 1 cc. of compound there are	0.915 cc. rubber
The value for rubber is	0.296 cal.

The rubber in the compound should therefore give 0.271 cal. Instead 0.418 cal. were obtained. Therefore, the reinforcing action per cc. of compound, calculated on the rubber contained in the compound, is  $0.418 - 0.271 = 0.147$  or about 0.15 calorie.

This value is called " $\Delta A$ " (Table II, column 3).

The other values given in Table II are calculated in a similar manner. The specific gravity of zinc oxide is taken as 5.6, that of gas black as 1.75.

TABLE I  
DATA AND CALCULATION OF BREAKING EXPERIMENTS

1	2	3	4	5	6	7	8	9	10
No. of Sample	Composition of Compound (% by Volume)	Ring No.	Weight of Ring in Grams	Sp. Gr. of Ring	Work of Rupture of Ring in Sq. cm. Surface (Fig. 8) Based on the Total Area of Compound in the Ring	Work of Rupture (According to Column 6) Based on 1 Cc. of Compound	Work of Rupture $A'$ in Calories Based on 1 Cc. of Compound	Rubber (not Reinforced) in 1 Cc. of Compound Would Lead One to Expect the Following Work of Rupture in Calories	Reinforcing Action $\Delta A$ , Which the Rubber Undergoes (Column 8 Minus Column 9)
1	100% raw rubber milled in the same way as the compounds	1	1.62	0.92	11.3	Ave. 6.3	0.296	0.296	...
		2	1.52		10.4				
		3	1.33		9.2				
		4	1.38		9.5				
2a	91.5% rubber 8.5% gas black	1	1.51	0.99	13.6	Ave. 8.9	0.418	0.271	0.147
		2	1.55		13.9				
								(91.5% of 0.296)	
2b	83% rubber 17% gas black	1	1.57	1.06	27.2	Ave. 17.1	0.805	0.246	0.559
		2	1.55		22.5				
								(83% of 0.296)	
5a	91.5% rubber, 8.5% zinc oxide	1	1.82	1.32	13.6	Ave. 10.5	0.493	0.271	0.222
		2	1.87		15.7				
								(Measurements not very certain)	

5b	83% rubber	1	2.45	1.69	? } 33.7 } 28.1 }	Ave. 24.5	1.13	0.246	0.884
	17% zinc oxide	2	2.20						
		3	2.10						
5c	74.5% rubber	1	3.10	2.11	30.6 } 35.8 }	Ave. 24.5	1.15	0.221	0.929
	25.5% zinc oxide	2	2.70						
5d	66% rubber	1	3.90	2.50	46.3 } 49.8 }	Ave. 31.5	1.47	0.195	1.275
	34% zinc oxide	2	3.75						

TABLE II  
DATA ON THE REINFORCEMENT AND HEAT OF WETTING OF UNVULCANIZED RUBBER COMPOUNDS

1	2	3	4	5	6	7	8
Composition % by Volume	A'/Cc. Compound	$\Delta A$ /Cc. Compound	U/Cc. Compound	U <sub>c</sub> /Cc. Filler	U <sub>c</sub> /G. Filler	U <sub>o</sub> /G. Filler	U <sub>o</sub> /Cc. Filler
Raw rubber	0.296	..	..	..	..	..	..
8.5% black	0.418	0.15	0.67	7.96	4.53	..	..
17 % black	0.805	0.56	1.03	6.08	3.47	about	about
25.5% black	...	..	1.35	5.25	3.03	11 cal.	19 cal.
34 % black	...	..	1.72	4.97	2.9	..	..
8.5% ZnO	0.493	0.22 (?)	..	..	..	..	..
17 % ZnO	1.13	0.88	1.51	8.84	1.58	about	about
25.5% ZnO	1.15	0.93	1.41	5.54	0.99	5 cal.	28 cal.
34 % ZnO	1.47	1.27	1.62	4.76	0.85	..	..

In order to make the calculations—which in themselves are quite simple—more intelligible, there are given in Table I the data from which are obtained the values given in Table II, columns 2 and 3, for the work of rupture  $A'$ , and the reinforcing ability  $\Delta A$ , which appear as results obtained in columns 8 and 10. The table is obtained from calculations similar to the one carried out in detail for compound No. 2a. The composition of the compounds is expressed in per cent. by volume. The relationship between per cent. by volume and per cent. by weight is obtained from the following formulas:<sup>13</sup>

$$(1) \quad f = \frac{100 F}{100 k - F(k - 1)}$$

$$(2) \quad F = \frac{100 k}{\frac{100}{f} + (k - 1)}$$

where  $f$  = % filler by volume,  $F$  = % filler by weight, and  $k = S_f/S_k$ ,  $S_f$  being the specific gravity of the filler, and  $S_k$  that of the medium, in this case rubber. The graph shown in Fig. 6, expressing the relationship of the above equations for a number of values of  $k$ , is a convenient means of orienting the two concentration expressions.

For other values of  $k$  similar curves may be easily interpolated, and for this purpose the intersection points of the curves with the abscissa are given from  $k = 1$  to  $k = 11$  up to  $F = 90$ .

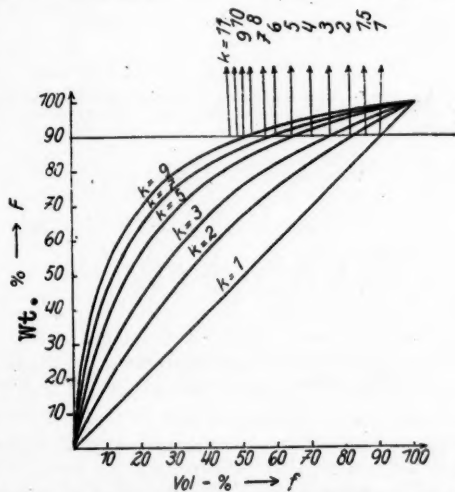


Figure 6—Conversion of % by Volume to % by Weight. ( $K$  = Sp. Gr. Filler/Sp. Gr. Rubber)

The graphical extrapolation of the value of  $U_c$  at a concentration of 0% of gas black, that is  $U_0$ , is shown in Fig. 7.

Table II gives in the first column the composition of the compound used in per cent by volume, in the second column the work of rupture  $A'$ , as shown by the Schopper machine in calories per cc. of compound, in the fourth the calorimetric value of the energy required to overcome the interfacial tension ( $U_c$ ) expressed

per cc. of compound, and in the fifth and sixth the value of this interfacial energy per cc. and per gram of filler.

The values given in the last two columns, 7 and 8 are graphically interpolated and consequently are accompanied by considerable uncertainty. They indicate what the magnitude of the reinforcing action of the particular filler would be at 0 concentration. From the decrease in the value of  $U_c$  with increasing concentration, it is seen that a filler, according to its surface energy, is utilized the less perfectly the larger the concentration of it in the compound; that is, at higher concentrations a large part of the filler acts only as ballast. The attainment of an "idea mixture,"<sup>14</sup> in which every particle of filler must be surrounded by rubber without the formation of "agglomerates" is therefore far removed from present-day practice. A measure of the extent to which a filler is utilized is given by the ratio  $U_c/U_0$ , which

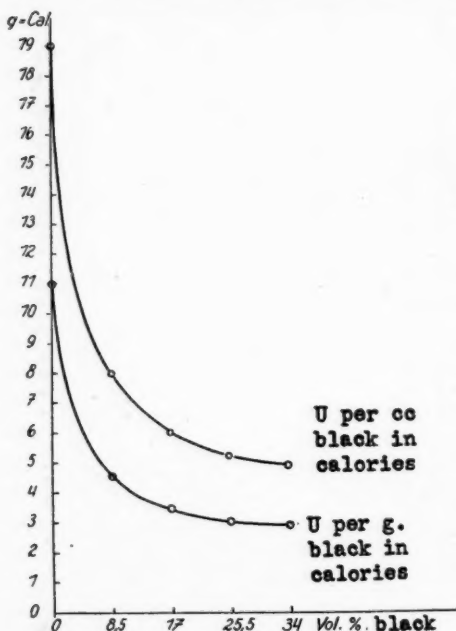


Figure 7—Dependence of Specific Heat of Wetting of Rubber/Gas Black Mix on Concentration of Black

for the gas black and zinc oxide above is as follows:

$\frac{U_c}{U_0}$ for	8.5	17	25.5	34 % by volume
Gas black	0.42	0.31	0.27	0.25
Zinc oxide	0.32	0.32	0.20	0.17

These figures indicate how incompletely—only one-half to one-fifth—the surface energy of fillers can be utilized. It is interesting that the value for  $U_0$  in the case of zinc oxide (about 28 cal./cc.) is larger than in the case of gas black (about 19 cal./cc.). Because of the coarser character of the zinc oxide, the capacity factor of its surface energy is smaller than that of the black. Its intensity factor, the surface tension between rubber and zinc oxide, must, therefore, be greater.

These results are given in the third column of Table II in still another way, namely, so that the heat of adhesion is based, not on 1 cc. of the filler, but on one cc. of the compound in question. It may be easily seen what the trend of the curve for this value of  $U$  must be. The surface energy presented per cc. of compound at a concentration of 0 and also at a concentration of 100% is 0, since in both instances no surface energy comes into play. With increasing content of filler the

total surface increases, but not in direct proportion, as with increasing concentration more and more of the filler loses its ability to act on the rubber due to the formation of agglomerates. The curve must therefore proceed from 0, pass through a maximum, and at a concentration of 100%, again return to 0.

It is very important that, in view of the aging of rubber, the physical and calorimetric values be obtained on compounds and rubber of the same age.

On comparing the reinforcing action of a filler with the size and intensity of its surface, it is easily seen that an analogous trend in the  $A$  curve must correspond to that of the  $U$  curve pictured. The reinforcing action of a filler on the work of rupture must therefore pass through a maximum at a definite concentration. Moreover, this characteristic demanded by the theory is possessed by the empirical curves of Wiegand, where the increase in the work of rupture is related to the concentration of filler.

An attempt may now be made to ascribe a value to the total surface tension in the system rubber/black. For this purpose we must know:<sup>15</sup> (1) the value  $A_0$  and (2) the average particle size of the filler.

The value  $A_0$ , which is the free surface energy available in the compound, cannot be obtained by direct measurement. However, it is possible to obtain some idea of its magnitude in another way. Table III below shows the values of the free and total surface energy in a few systems.

TABLE III

THERMODYNAMIC DATA FOR THE FORMATION OF 1 SQ. CM. OF SURFACE

(+ $A$  = work done by the system, + $Q$  = heat consumed by the system, + $U$  = decrease of total energy)

System	Temperature $T$ (Abs.)	$t$ (Cels.)	$A$ erg	$Q$ erg	$U$ erg	$A/U$	$\frac{dA}{dT}$ in % of $A$
Benzene	278	5	-30	+29	-59	0.51	-0.35
Benzene	350	77	-23	+35	-58	0.39	-0.46
Water	293	20	-74	+45.4	-119.4	0.62	-0.21
Aniline	293	20	-43.8	+32.2	-76	0.58	-0.25
Mercury	288	15	-465	+88.5	-553	0.84	-0.07
Water/petroleum	289	16	-48	+69.4	-117.4	0.41	-0.50
Mercury/benzene	293	20	-342	+401	-743	0.46	-0.40

As the foregoing table indicates, the ratio  $A/U$  in all these systems is in the neighborhood of 0.5. Therefore, in order to obtain a general idea we may assume that this holds true of the system rubber/filler, at least to the same order of magnitude. This assumption may be corroborated in another way. In zinc oxide compounds the reinforcement  $A$  per cc. is 0.22, 0.88, 0.93, and 1.27 calories based on compounds containing 8.5, 17, 25.5, and 34% by volume of ZnO. The heat of adhesion of these compounds per cc. is

17	25.5	34	% by volume
1.51	1.42	1.62	cal.

which gives

$A/U =$	0.58	0.66	0.78.
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If the reinforcing action is due exclusively to the free surface energy, and if thermodynamic considerations are strictly fulfilled, then for a given system  $A/U$  must be independent of the concentration. The fact that the work of rupture increases faster than the free surface energy is apparently due to its complex character. In any case it is composed not only of the effect of the free surface energy, but to an ever-increasing extent, the frictional work, which is the more noticeable the less

surface the filler has in common with the rubber, thereby acting only as ballast. If one extrapolates the above values to 0 concentration, one obtains in the case of an infinitely diluted ZnO dispersion  $A/U = 0.5$ . In the case of gas black the value of  $A/U$  should be somewhat smaller, though the figures permit no safe extrapolation.  $A/U$  for  $c = 0$  should be about 0.2.

Some investigations on the average size of gas black particles have been made by Prof. Tibor Peterfi (private communication). From them one can infer that the average particle radius of the gas black examined must be in the neighborhood of  $0.025\mu$ . The internal surface of the gas black particles appears to play no noticeable part; for, if the particles were very much agglomerated, the heats of wetting of the various blacks could not increase with the degree of fineness, as is actually the case. If one assumes that  $A_0/U_0$  in the case of gas black is about 0.2, one obtains for  $A_0$  about  $-3.8$  to  $-4$  calories per cc. of black, and the following calculation can be made merely for orientation purposes.

One particle weighs  $4/3 \cdot 3.14 \cdot (2.5 \cdot 10^{-6})^3 \cdot 1.75$  g. Therefore 1 g. of black contains  $3.10^{18}/4 \cdot 3.14 \cdot 15.625 \cdot 1.75$  or  $8.73 \cdot 10^{15}$  particles.

One cc. of black contain 1.75 times as many or  $15.3 \cdot 10^{15}$  particles. The surface of one particle is  $O = 4 \cdot 3.14 \cdot 6.25 \cdot 10^{-12}$  sq. cm. and the total surface of 1 g. of black  $O = 6.86 \cdot 10^5$  sq. cm. and the total surface of 1 cc. of black  $O = 1.2 \cdot 10^6$  sq. cm. Then if  $A_0$  is set at about  $-4$  cal./cc. of black as shown above, there follows:

$$\begin{aligned} A_0 &= - \frac{4}{1.2 \cdot 10^6} \text{ cal./sq. cm.} \\ A_0 &= - 3.3 \cdot 10^{-6} \text{ cal./sq. cm.} \\ A_0 &= - 140 \text{ ergs per sq. cm. black.} \end{aligned}$$

Even if this value is 100% in error, still it seems plausible and acceptable at least to the order of magnitude given.<sup>16</sup>

The main source of error in the above calculations is in the uncertainty of the value  $A_0$ . However, this difficulty can be overcome in another way, provided that there are available three types of zinc oxide which have received similar chemical treatment, and which differ only in degree of fineness.<sup>17</sup>

From the relationship between the heats of wetting of the three powders a conclusion may be drawn as to their relative surface areas.<sup>18</sup> If, then, a series of compounds of rubber and zinc oxide are investigated, and all three extrapolated to 0 concentration, there are obtained three  $U_0$  values per gram or per cc. of the three types, such as coarse, medium, and fine zinc oxide. Now if the surface presented by a gram of filler is  $f$ ,  $nf$ , and  $mf$ , respectively (where only  $n$  and  $m$  need be known), and if  $k$  is the fraction of  $U_0$  represented by  $A_0$  (which in the above example is taken as about 0.2 for gas black), the following three equations are obtained:

$$(I) \sigma \cdot f = k \cdot U_1; (II) \sigma \cdot nf = k \cdot U_2; (III) \sigma \cdot mf = k \cdot U_3.$$

In these three equations the unknowns are: (I) the surface tension  $\sigma$ , which can be considered as practically the same in all three cases in view of the similar origin; (II) the factor  $k$ , and (III) the surface  $f$  of a gram of No. I. The three equations therefore may be solved.

If one could, on the basis of microscopic measurements, give a reliable expression of the absolute value of  $f$ , then of course two equations would suffice to calculate the surface energy. Finally, though it could hardly be possible, if  $k$  could be determined experimentally with certainty from the work of rupture, then the goal could be reached with one of the three equations, as attempted above. In any case, by determining the value of  $U_0$  very carefully in compounds containing a very low concentration of filler, one comes very close to obtaining as certain as possible an extrapolation of the value of  $U_0$ .



In regard to the calculation of  $U$  from calorimetric data according to the scheme given above, it may be pointed out that this calculation may be carried out with greater reliability the fresher the rubber and the compounds are that are subjected to calorimetric measurement. It can easily be seen that a relatively large error in the determination of the heat of swelling of rubber has little effect on the final result, because the value for rubber is so small that it can be considered as practically nil. If compounds or rubber are used which have been lying in storage for a long time, say a year, a very annoying effect occurs; namely, the heat of swelling of rubber increases markedly with increasing age. Rubber, which when new gave a value of 0.15 calorie per gram, gives over 4 calories per gram after a year.<sup>19</sup> The heat of swelling of compounds increases with age in exactly the same way. In that case a small percentage of error in measuring the heat of swelling becomes so important that in some cases entirely misleading results are obtained. This may be shown by the following example.

A compound was used which contained 28% by weight of gas black and 72% by weight of rubber. The value of the heat of swelling of rubber was about -4.0 calories per gram. Since the accuracy of the method was only 5%, let the value be 4.0 cal./g. in one calculation and 4.2 cal./g. in the other. The heat of wetting of the black was +0.27 cal./g., and the heat of swelling of the compound in three experiments averaged -3.70 cal./g.

I	
0.28 g. black gave	+0.08 cal.
0.72 g. rubber gave	-2.88 cal.
1.00 g. of compound, therefore, should give	-2.80 cal.
Instead there were obtained	-3.70 cal.
The reinforcing effect was therefore	+0.90 cal.

This reinforcement was effected by 0.28 g. of black; therefore its value amounted to 3.2 calories per gram of black.

II	
0.28 g. black gave	+0.08 cal.
0.72 g. rubber gave	-3.02 cal.
1.00 g. of compound, therefore, should give	-2.94 cal.
Instead there were obtained	-3.70 cal.
The reinforcing effect was therefore	+0.75 cal.

This reinforcement was effected by 0.28 g. of black; therefore its value amounted to 2.57 calories per gram of black.

At first an attempt was made to meet this unpleasant phenomenon by swelling a piece of rubber and later removing the solvent completely by means of an air pump. It seems reasonable to expect that the aging process would be made reversible in this way. On the contrary it was found that swelling cannot dissolve the molecular aggregates formed on aging. The second swelling gave the same result as the first.

However, when another sample that had been aged was milled up again, it gave the same value on swelling which one would expect if the rubber were new. The mechanical effect of mastication combined with the high temperature completely dissolved the bonds between the rubber molecules due to aggregation, though swelling could not do so.

For the purpose of comparing a series of blacks, compounds were on hand which had been aged for about a year. Unfortunately it was not possible to freshen them up again by milling because they had been frictioned onto wire netting for the purpose of obtaining better heat conductivity. Therefore there was nothing

else to do but to increase the reliability of the measurements by increasing the number of parallel experiments. The average of the heat of swelling of the rubber used in 12 determinations was  $-4.2$  cal./g. of rubber.

The compounds all contained 28% of gas black. The results of the experiments are compiled in the following table:

Black No.	Heat of Wetting of the Black in Cal./G.	Heat of Swelling of the Compound in Cal./G.	Surface Energy (in Calories) Calculated on	
			1 G. Black	1 Cc. Compound
1	+0.27	-3.67	2.57	4.49
2	+0.66	-3.25	1.94	3.39
3	+0.77	-3.61	3.89	6.81
4	+1.32	-4.67	7.22	12.63
5	+3.6	-4.38	8.4	14.7

In technical value as reinforcing fillers these blacks range about in the order given in the table. Naturally strict proportionality does not exist nor is to be expected, for the dissolution of the surface force at the boundary rubber/black by swelling is of course very different from the dissolution of the same force by mechanical rupture.

### Notes

<sup>1</sup> *Dissertation*, Giessen, 1928.

<sup>2</sup> *Kolloidchem. Beihefte*, **26**, 439 (1928).

<sup>3</sup> *Ibid.*, **26**, 439 (1928).

<sup>4</sup> Because of the indefinite character of the rubber samples, the electrical calibration of the calorimeter did not need to be carried out with excessive accuracy. Comparison with a standard instrument sufficed.

<sup>5</sup> Regarding the use of a nomograph for calculating the data of the calibration, see C. L. Nottebohm, *Dissertation*, Giessen, 1930.

<sup>6</sup> Roth, *Phys.-chem. Übungen*, 4th ed., 1928, p. 73.

<sup>7</sup> Twiss, *Annual Reports of Applied Chemistry*, **4**, 324 (1919).

<sup>8</sup> Wiegand, *Trans. Inst. Rubber Industry*, **1**, 141 (1925). Hock, *Handbuch der Kautschukwissenschaft*, p. 557.

<sup>9</sup> The base mix consisted of 100 vol. rubber, 3 vol. litharge, and 2.5 vol. sulfur.

<sup>10</sup> The per cent. by volume of filler is based on the volume of rubber contained in the compound, and therefore expresses the volume of filler corresponding to 100 vol. of rubber.

<sup>11</sup>  $U_c$  is the heat of wetting of a gram of filler at a concentration  $c$ .  $U_0$  is the extrapolated value for  $c = 0$  which would be obtained with perfect wetting. The concentrations are calculated in % by volume.

<sup>12</sup> For calculations of this nature, see Hock, *Kautschuk*, **3**, 314 (1927).

<sup>13</sup>  $\frac{F}{S_f} + \frac{100 - F}{S_k} = V_m$ , where  $V_m$  is the volume of 100 parts by weight of compound. If the volume of filler is  $\frac{F}{S_f} = V_f$ , then by definition  $f = \frac{V_f \cdot 100}{V_m}$  in % volume.

The above equations are then obtained by substitution.

<sup>14</sup> Hock, *Kautschuk*, June, 1927.

<sup>15</sup> Hock, *Z. Elektrochem.*, **34**, 662 (1928) and *Kautschuk*, June, 1927 and August, 1928. Hock and Fromandi, *Ibid.*, **5**, 81 (1929) and *Handbuch der Kautschukwissenschaft*, p. 562. This method of calculation should first of all indicate the manner in which an indisputable figure may be obtained. The assumption of an inner surface, particularly, has been disregarded. This assumption may be made with greater reliability in the case of zinc oxide, and the zinc oxide compounds were investigated in the purely calorimetric way described for this reason. In the case of various blacks of different degrees of dispersion, the existence of chemically identical surfaces is not assured. The chemical nature of the surface has a decisive bearing on the surface energy.

<sup>16</sup> For the determination of the surface tension between solid bodies see Bakker, *Handbuch der Physik*, **6**, 256 (1928).

<sup>17</sup> Hock, *Z. Elektrochem.*, **34**, 662 (1928). See also note 14.

<sup>18</sup> Bostroem, *Dissertation*, Giessen, 1927. Hock and Bostroem, *Kautschuk*, Jan., 1927.

<sup>19</sup> The tensile increases in the same way. See Le Blanc and Kröger, *Handbuch der Kautschukwissenschaft*, p. 477.

# Chemical Adsorption Studies of Rubber Fillers and Rubber Compounds

## Communication No. I

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The evaluation of a filler, especially its behavior in a compound, depending on the special considerations to be met, is now judged almost entirely by a systematic study of its physical properties in the compound itself. Results and numerical values thereby obtained, depending on the character of the compound, in the majority of cases permit of no generalizations. However, they do permit certain conclusions which indicate the choice of a particular filler as suitable from a technical point of view.

Wiegand<sup>1</sup> obtained some insight into the complicated relationships involved, in the following manner. By a systematic study of the "proof resilience" or work of rupture of a base mix which is characteristically affected by the addition of increasing volumes of various fillers, he was able to show that the reinforcing action of finely divided fillers is primarily a function of their higher degree of dispersion and of the greater surface in common thereby obtained—a finding which was confirmed by the work of North.<sup>2</sup>

If, as suggested by Wiegand,<sup>3</sup> the reinforcing action is considered as a function of the amount of filler, introducing the well-known value of "A" and the technically important " $\Delta A$ " function, a very clear picture of these relations is obtained.

However, the average particle size of the filler, whose measurement was suggested by these experiments, was almost never, as we know, sufficient explanation in itself of its value and behavior in compounding. Other factors play a part which are of prime and decisive importance, and whose exact numerical evaluation involves difficulties that are not insignificant. Particularly the determination of the particle size of gas black, for example, which is attended by considerable difficulty, does not permit any definite conclusions as to the chemical and physical nature of the filler surface<sup>4</sup> on which the "activity" or "inaactivity" depends primarily.

In accordance with Pouillet's<sup>5</sup> observation that the wetting of a dry powder is accompanied by a heat effect which is directly proportional to the surface activity, Hock, Boström, and Hartner<sup>6</sup> have worked out a calorimetric method which permits a relative evaluation of rubber fillers by obtaining their interfacial energies.

In this connection the question was asked, could not the adsorption powers of a filler and its numerical evaluation be utilized for comparison, especially as the necessary procedure would permit of speedy execution of experiments which later would be critically examined with respect to the most important phenomena more or less affected by adsorption.

It is known that various blacks differ considerably in their reinforcing action and their effect on the degree of cure. This difference characterizes not only the principal varieties themselves, but is often evident within the individual groups.

The reason for this has not thus far been satisfactorily shown, though the very complicated relations which here exist offer the least difficulty to the formulation of laws of general applicability.

In evaluating a gas black, chemical analysis is of only limited value, as it permits no direct conclusions regarding the behavior of the black in the compound, the effect on aging being one of the few exceptions. When gas black, acetylene black, and lamp black are analyzed in the same way, it is found that acetylene black is the purest chemically, lamp black showing a somewhat lower degree of purity. However, in the majority of cases the amount of impurities is so small that no conclusions may be drawn directly as to the worth of a black or its behavior in a compound, even if there is a possibility that the impurities are present in the gas black particles in an unusually fine state so that they can bring about special surface or catalytic effects. Moreover, there is the fact that different shipments of a given black show not unessential differences in analytical composition, somewhat nullifying the limits for the amount of impurities (for example, iron) which characterizes various types of black in general.

On the other hand it is not possible to predict from direct measurement of particle size the behavior of a gas black in a given compound or the extent of its reinforcing action. The following table<sup>7</sup> shows some of the characteristic physical constants involved.

TABLE I  
PHYSICAL DATA ON THE RELATIVE PARTICLE SIZE OF THE THREE IMPORTANT TYPES OF BLACK

Type of Black	Average Volume per Gram, Cc./G.	Average Particle Size, Direct Measurement	Particle Size in 50% Alcohol	Brownian Movement
Gas black	3.7	0.2 $\mu$	4	None
Acetylene black	5.0	...	2	Weak
Lamp black	9.6	0.1 $\mu$	1	Very marked

The figures for lamp black would indicate a superior position; but in reality the exact opposite is the case, as we know. Gas black stands supreme, at least considering its ability to consume energy, which interests us primarily as a criterion of its reinforcing action.

In the following table the real conditions are expressed more clearly by the comparison of the specific surfaces according to Wiegand<sup>8</sup> and the relative surface magnitudes according to Hock and his co-workers<sup>9</sup> as obtained from the heats of wetting.

TABLE II  
RELATIVE SIZE OF PARTICLE SURFACE OF GAS BLACK AND LAMP BLACK

Type of Black	Specific Surface (Sq. In. per Cu. In.)	Average Heat of Wetting, Cal./G.	Relative Size of Particle Surface
Gas black	1,905,000	4.0	140
Lamp black (Oil black)	1,524,000	1.1	40

In this connection it might be interesting to study further the evaluation and behavior of blacks in compounds from a chemical adsorption point of view. The working hypothesis on which these experiments are based is that the chemical and physical nature of the surface is the same in all blacks of technical importance, an assumption for which there is, to be sure, no absolute foundation, but which

has thus far appeared practically certain, apart from a single exception which will be mentioned later.

The details of the procedure were as follows.<sup>10</sup> To six Erlenmeyer flasks of 200 cc. capacity there were added the following quantities of dilute acetic acid of the normality indicated.

No.	1	2	3	4	5	6
Cc.	150	150	150	125	110	105
N	0.06	0.12	0.25	0.5	1	2

Before the adsorbent was added, which was 15 g. of black in each case, 50 cc. were pipetted off from each of flasks 1, 2, and 3, 25 cc. from flask No. 4, 10 cc. from flask No. 5, and 5 cc. from flask No. 6; and in each case the acetic acid content was determined by titration with 0.5 N KOH, using phenolphthalein as an indicator. The quantity of liquid remaining in the flask was therefore 100 cc. in each case. The black under examination in each case was then added in the quantity mentioned, and the flask shaken from fifteen to twenty minutes by hand or in a shaking machine so as to obtain a rapid and equal change of concentration within the whole system.

The following table indicates the speed with which the adsorption equilibrium<sup>11</sup> was reached in the case of a gas black. (Concentration of acetic acid in all four flasks = 1 N. In each case 10 cc. were pipetted off for titration.)

TABLE III

DETERMINATION OF THE SPEED OF ADSORPTION OF ACETIC ACID BY CARBON BLACK

Determination of Equilibrium after	<i>c</i>	<i>c - x</i>	<i>x</i>	$\Delta x$
0 hours	200.00	187.80	12.20	0.00
3 hours		187.80	12.20	0.00
6 hours		187.80	12.20	0.02
24 hours		187.78	12.22	

*c* = initial concentration in cc. 0.5 N KOH per 100 cc. solution.

*c - x* = equilibrium concentration in cc. 0.5 N KOH per 100 cc. of filtrate following adsorption.

*x* = quantity adsorbed in cc. 0.5 N KOH per 100 cc. solution.

The table shows that adsorption equilibrium was reached quickly, so that immediately after shaking and allowing the flask to stand a short time the contents could be filtered off through a dry filter. In determining the equilibrium concentration the filtration was made in this way and the aliquot pipetted off from the filtrate.

The following table represents a series of experiments with a gas black as the adsorbent.

TABLE IV

ADSORPTION OF ACETIC ACID BY CARBON BLACK

No.	<i>c</i>	<i>c - x</i>	<i>x</i>	log ( <i>c - x</i> )	log <i>x</i>
1	12.66	9.60	3.00	0.984	0.478
2	24.84	20.40	4.44	1.311	0.647
3	49.48	43.00	6.48	1.634	0.812
4	98.44	90.25	8.19	1.957	0.914
5	200.00	187.80	12.20	2.251	1.087
6	396.40	380.00	16.40	2.580	1.215

$$K = 3.25 \quad n = 0.48$$

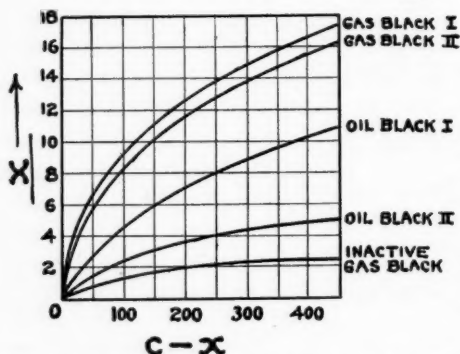


Figure 1—Isotherms of the Adsorption of Acetic Acid on Blacks

In Fig. 1 the results obtained with various blacks are given in the form of isotherms in the  $x/(c-x)$  diagram.

These "concentration curves of adsorption" first of all show in general the trend characteristic of adsorption; the quantity adsorbed tends toward a maximum, the "adsorption maximum." The characteristic initial portion of the curves shows that conditions closely fulfil the requirements of Freundlich's formula

$$x = K(c-x)^n$$

$K$  and  $n$  being constants, which is pretty generally<sup>12</sup> applicable to adsorption phenomena in dilute solution.

Further, the curves given in Fig. 1 show that the isotherms obtained with the various blacks have a different, sharply characterized trend. The difference between active and inactive gas black especially is manifest, while the oil blacks occupy an intermediate position.

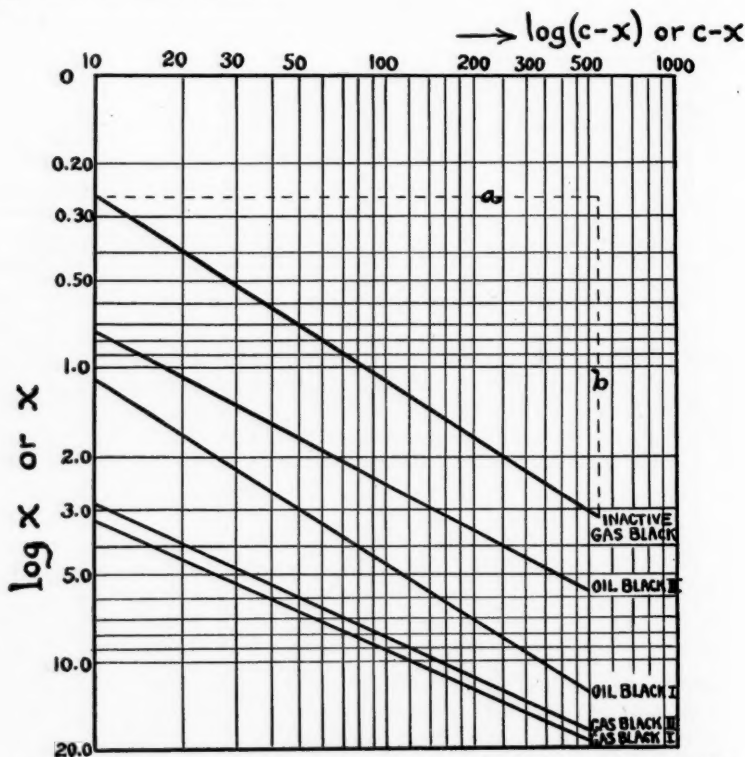


Figure 2—Isotherms of the Adsorptive Capacity of Acetic Acid on Blacks. The Logarithmic Form of the General Adsorption Equation



The logarithmic form of the above formula<sup>13</sup>

$$\log x = \log K + n/\log (c - x)$$

is recognized as an equation of a straight line, and the change of Fig. 1 to the corresponding logarithmic form in Fig. 2 shows the characteristic differential power of adsorption of the blacks still more clearly.

Figure 2 affords a means of determining the numerical value of  $K$  and  $n$ .  $\log K$  is the distance which the corresponding straight line cuts off on the  $\log x$  axis, and  $n$  is the tangent of its angle of incidence, i. e.,  $a/b$ , which for the sake of accuracy is taken as large as possible.

These constants, especially the  $K$  value, afford a method, as shown by Table V, which permits a good, numerical evaluation of carbon blacks, particularly with respect to their behavior in a compound.<sup>14</sup>

TABLE V  
K VALUES OF A FEW CARBON BLACKS

Type of black	K
Gas black No. 1	3.25
Gas black No. 2	2.90
Inactive gas black	0.26
Oil black No. 1	1.10
Oil black No. 2	0.74

To correlate the various blacks in the laboratory in most cases it is sufficient to obtain a factor expressing the power of adsorption in a definite concentration of acetic acid, say 1  $N$ , in the manner described, as shown in Table VI.<sup>15</sup>

TABLE VI  
ADSORPTION OF 1  $N$  ACETIC ACID BY CARBON BLACK. 15 G. BLACK; 100 CC. LIQUID

Type of Black	$c$ Initial Concentration in Cc. 0.5 $N$ KOH per 100 Cc. Solution	$c - x$ Equilibrium Concentration Following Adsorption in Cc. 0.5 $N$ KOH per 100 Cc. Filtrate	$x$ Quantity Adsorbed in Cc. 0.5 $N$ KOH per 100 Cc. Solution
Gas black No. 1	200.00	187.80	12.20
Gas black No. 2		189.00	11.00
Inactive black		198.20	1.80
Oil black No. 1		193.20	6.80
Oil black No. 2		196.50	3.50

The translation of these results into the technical behavior of the blacks on compounding is reserved for a later publication, in which all phenomena having more or less bearing on the case will be discussed from a chemical adsorption point of view.

#### Notes

<sup>1</sup> *India Rubber J.*, **60**, 379, 423 (1920).

<sup>2</sup> *India Rubber World*, **63**, 98 (1920).

<sup>3</sup> *India Rubber J.*, **70**, 11 (1925).

<sup>4</sup> Unfortunately we have no method of determining the total surface, outer as well as inner, provided of course that an inner, active surface is usually present.

<sup>5</sup> *Ann. chim. phys.*, **32**, 141 (1822).

<sup>6</sup> *Kautschuk*, **3**, 207 (1927); Boström, *Dissertation*, Giessen, 1927.

<sup>7</sup> Dawson, *Trans. Inst. Rubber Industry*, **5**, 84 (1929).

<sup>8</sup> *Loc. cit.*

<sup>9</sup> *Loc. cit.*

<sup>10</sup> Ostwald-Wolski, *Kleines Prakt. d. Kolloidchemie*, 2nd ed., p. 100, 1921.

## Notes (Continued)

<sup>11</sup> As the temperature coefficient of adsorption at a liquid solid boundary is relatively small, the determination can be carried out, as in the present case, without the help of a thermostat, for example at room temperature.

<sup>12</sup> In adsorption in gases as well as in solutions, saturation is to be expected; however, the formula does not take saturation into account, even though by varying it can to some extent be fitted to the form of the curve in a given case.

<sup>13</sup> The logarithmic drawing paper of Schleicher and Schüll is especially suitable.

<sup>14</sup> The same principle holds for all fillers. Work in this direction is already in progress, and the results are being reserved for later publications.

<sup>15</sup> Similar results are obtained in the adsorption of iodine or quinine sulfate, the concentration of which is determined either volumetrically or by determining the degree of turbidity using Mayer's reagent (potassium mercury iodide) or even by titration. (*Lunge-Berl*, 7th ed., 3, p. 925).

# A Study of the Vapor-Pressure Diminution of Rubber Jellies

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Although swelling-pressure measurements have been carried out by Posnjak (*Kolloidchem. Beihefte*, 1912, 3, 417) on rubber, and theories have been put forward whereby the swelling pressure may be calculated from the vapor-pressure diminution of the solvents in the jellies, no measurements of the latter value exist (*Idem, Ibid.*; Katz, *Ibid.*, 9, 106 (1928)).

Rubber seems to be suitable for investigations of the nature of swelling, because it combines with many organic fluids of diverse properties, and without the action of reagents, may be made to yield jellies of widely different consistency (according to the previous mechanical treatment of the natural product). It has already been shown that the consistency of the final "solution" of rubber has no influence on its vapor pressure (Stamberger, *Rec. trav. chim.*, 47, 316(1928)).

Measurements are now recorded of the vapor-pressure diminution of rubber jellies in three solvents, *viz.*, benzene, chloroform, and carbon disulfide, and particularly at low concentrations of rubber, so that comparison with the behavior of molecular disperse solutions may be made.

The origins of the samples of rubber used were as follows: (1) Isolated from pure latex, freed from the protein content by centrifuging and subsequent dilution (acetone-soluble, 2.2; N, 0.12%). (2) Dutch plantation rubber (first latex crepe) of 1926 (acetone-soluble, 3.0; N, 0.14%). (3) Plantation rubber from Ceylon (acetone-soluble, 3.6; 3.6; N, 0.09%). (4) Rubber No. 2 in over-masticated conditions purified by solution in benzene and precipitation with acetone (acetone-soluble, nil; N, 0.03%). (5) Rubber No. 3 in over-masticated condition. These samples, with the exception of No. 4, were used without further treatment after being dried over sulfuric acid in a vacuum desiccator for 14 days, and *no difference was found in their behavior*. All the values were reproducible after an interval of 2 years. The vapor pressure was determined by two methods: (1) that of Gay-Lussac-van Bemmelen, which is generally used for these determinations (compare Katz, *Ergebnisse der exakten Naturwissenschaften*, 3, 317 (1924)), solutions of paraffin oil of an average molecular weight of 425 being used as fluids of known vapor pressure; (2) a direct method in a modified Bremer-Frowein tensimeter. Both methods gave practically identical results. The direct measurement could not be carried out when the vapor-pressure lowering was less than 2 mm., because of experimental difficulties.

*Method 1.*—Solutions obtained with the above-mentioned paraffin oil\* of a concentration of about 2-50% were used. The vapor pressures of the solutions of low concentration (up to 10%) were calculated from the ebullioscopically determined molecular weight of the paraffin oil (425) by means of Raoult's formula  $(p_0 - p_1)/p_0 = n/(N + n)$ . Above this concentration the differential vapor pressure was determined in a tensimeter (shown in Fig. 2), which was also used for measurement of the vapor pressure of jellies. From the results given in Table I

\* A commercial product was used consisting of a mixture of paraffin hydrocarbons.

it is seen that the values calculated from the molecular weight agree with those obtained directly, and if the relative vapor pressure is plotted against the concentration of paraffin oil in the solution, a linear relationship holds up to a concentration of about 40%. These results are in agreement with recent investigations on the validity of Raoult's laws (Bancroft and Davis, *J. Phys. Chem.*, **33**, 361 (1929)). All the measurements were carried out in a thermostat at  $25^\circ \pm 0.005^\circ$ , and pressures were recorded in mm. of mercury.

TABLE I

 $p_0 = 90$  mm.

Paraffin, G./100 G. Solution	$p_0 - p_1$	$(p_0 - p_1)/p_0$		Paraffin, G./100 G. Solution	$p_0 - p_1$	$(p_0 - p_1)/p_0$	
		Calc.	Found			Calc.	Found
2.47	...	0.0042	....	26.5	5.6	0.0617	0.0624
5.0	...	0.0106	....	49.7	14.0	0.159	0.154
9.1	2.2	0.0241	0.0242	60.0	18.2	0.220	0.202
13.0	3.0	0.0348	0.0334	67.0	24.2	0.275	0.268

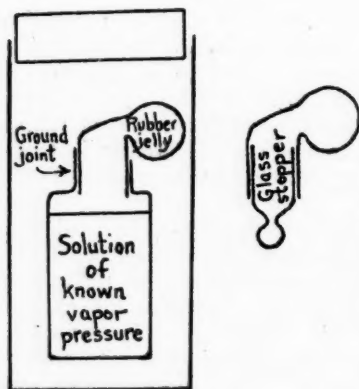


Figure 1

For this type of vapor-tension measurement of jellies, Wolff and Buchner (*Z. phys. Chem.*, **39**, 271 (1915)) point out the necessity of decreasing the vapor space to a minimum. It is also necessary, in order to obtain equilibrium quickly, to make the distance between liquid and jelly as small as possible. The arrangement shown in Fig. 1 was used for this purpose. To minimize the effect of fluctuations in the temperature of the thermostat, the whole apparatus was enclosed in a tube which was closed with a rubber bung and immersed in water.

0.2–0.5 gram of rubber was weighed into the stoppered bulb, the stopper was removed and the bulb connected by a ground glass joint with the vessel containing the solvent of known tension. From time to time (every 10 days) the bulb was disconnected, closed, and weighed. When no further increase of weight was noticeable, the tension of the jelly was identical with that of the liquid. From the increase of weight and the weight of rubber present initially the concentration of rubber in the jelly at a given vapor pressure can be calculated. The time necessary to obtain equilibrium was different with liquids of different tensions: When the vapor pressure lowering in the jelly was small, 3–4 months were required, but with greater differences about 3–4 weeks sufficed.

The apparatus for the direct determination of differential vapor pressure as well as for the determination of the vapor pressure lowering of the paraffin oil solutions, is shown in Fig. 2. For the latter, the pure liquid was poured through a side tube into one of the bulbs, and the solution of paraffin oil of unknown tension into the other. Both bulbs were cooled with liquid air, and the side tubes sealed. The apparatus was evacuated by means of a Langmuir high-vacuum pump (the usual precaution being taken to condense the vapor before it reached the pump). The connection with the vacuum was then closed by a mercury trap, the condenser filled, and the liquids in the bulbs were allowed to become warm slowly. The filling in the upper part of the condenser was solid carbon dioxide, and in the lower

part a freezing mixture (in the case of benzene) or acetone-carbon disulfide (in the case of chloroform or carbon disulfide).

To free the liquids completely from dissolved gases, they were kept for about 2 hours under vacuum, the whole system was then re-evacuated by a water pump, and the liquids in the bulbs were heated under reflux for 12 hours in a water-bath. It was necessary to use small amounts of liquid, about 10 cc. in large bulbs, for otherwise when it became air-free its boiling was accompanied by violent splashing. The liquid was then cooled to about  $-5^{\circ}$  and the system was evacuated by the high-vacuum pump for an hour, the liquid being further cooled with liquid air; the connection with the pump was closed and the liquids were allowed to attain room temperature and kept for 12 hours under vacuum. In the case of benzene, a further evacuation and 24 hours' standing were required. The necessity for the foregoing precautions may be illustrated by the fact that a liquid which had not been thus freed from dissolved gases gave a vapor pressure 15 mm. higher than after such treatment.

The air-free liquids were cooled again with liquid air, and the tube (which had naturally a capillary part) was connected with the vacuum, and gently warmed; the glass being now gas-free, the apparatus was sealed. The mercury, which had been previously boiled in a vacuum, was poured from the container connected with the manometer by gently tilting the apparatus, and the whole was put into a glass thermostat. The differential vapor pressure was read on the manometer with the aid of a cathetometer. Usually, no further change in the meniscus of the mercury was observed after 2 hours' standing in the thermostat, but if the liquids had not been completely free from gases a small further movement of the meniscus was noticed.

*Method 2.*—When the tension of the rubber jelly was to be determined, two bulbs instead of one were used on the one side. In the one connected with the condenser a known weight of the solvent was placed, and in the other, the dry rubber itself. The liquids were cooled and evacuated as described above, and the bulb with the dry rubber was heated to  $50^{\circ}$ . In this manner hardly any liquid condensed on the rubber, even when the liquid in the first bulb was boiled. As it was impossible to make a rubber jelly air-free, it was necessary to start from the dry rubber and liquid separately.

When the liquids had been again freed from gases, as described above, the apparatus was sealed, and the contents of the first bulb were poured into the second by tilting the apparatus, the contents of the third bulb being kept frozen during this operation. The apparatus was placed in a thermostat after the manometer had been filled with mercury. After 48 hours the whole of the solvent had been uniformly absorbed by the rubber, no further change in the meniscus occurred, and

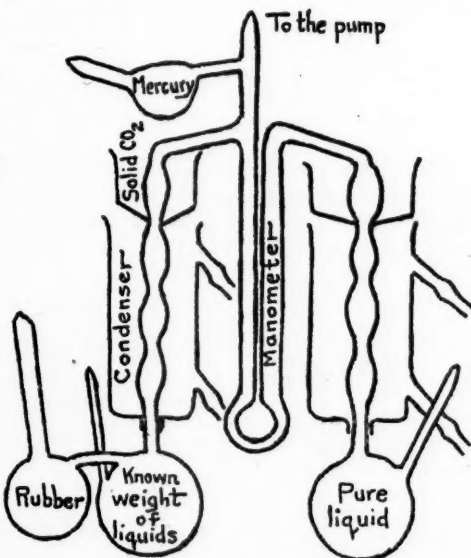


Figure 2

the differential vapor pressure could be measured. Although every precaution was taken in condensing the liquid when it was boiled, small amounts escaped and condensed in the retainers cooled with liquid air before the pumps. It was therefore necessary after every measurement to determine the concentration of the dissolved phase in the bulb directly by cutting off the second bulb, weighing it, evaporating the volatile liquid, and re-weighing the bulb.

The values given in Table II show the differences between the samples. The experimental error is estimated to be about 7%. Table III and Fig. 3 give the mean results obtained from 6-10 determinations in each case.

TABLE II  
Concentration of Rubber (% by Wt.) in Samples\*

Solvent	$\frac{p_0 - p_1}{p_0}$	1		2		3		4		5	
$C_6H_6$	0.0241	31.4	34.2	32.5	33.0	32.3	31.0	30.8	33.0	32.6	32.0
$C_6H_6$	0.154	55.0	54.8	56.5	54.2	58.0	56.0	54.0	56.2	55.6	54.0
$CHCl_3$	0.014	15.9	16.4	16.2	17.4	15.2	16.4	16.5	16.7	14.9	16.8
$CHCl_3$	0.278	58.1	55.5	55.0	57.3	56.8	56.0	58.2	57.1	56.2	57.0

\* Two determinations are given in each case.

Freundlich and Posnjak (*Kolloidchem. Beihefte*, 3, 445 (1912); see also Katz, *loc. cit.*) derived a formula  $P = -RT/MV \cdot \log p_1/p_0$  for calculating the swelling pressure from the vapor-pressure lowering. Figure 4 gives a comparison of the results thus calculated with the values determined by Posnjak.

TABLE III

G. of Solvent per 100 G. of Rubber	Concn. of Rubber (G./100 G. of Jelly)	G.-Mols. of Solvent per 100 G. of Rubber	$\frac{p_0 - p_1}{p_0}$
Solvent: Benzene; $p^{25^\circ} = 91$ mm.			
350	22.2	4.5	0.0042
280	26.3	3.6	0.0106
210	32.3	2.7	0.0241
190	34.5	2.4	0.0348
130	43.5	1.6	0.0617
76	56.8	0.9	0.154
55	64.5	0.7	0.220
50	66.7	0.6	0.278
Solvent: Chloroform; $p^{25^\circ} = 200$ mm.			
850	10.5	7.5	0.0034
520	16.1	4.3	0.0146
403	19.8	3.3	0.0258
237	29.6	2.0	0.0680
174	36.5	1.4	0.105
100	50.0	0.8	0.201
75	57.0	0.6	0.278
Solvent: Carbon disulfide; $p^{25^\circ} = 480$ mm.			
525	16	6.9	0.0044
420	19.4	5.5	0.0060
310	24.4	4.1	0.0167
210	32.8	2.7	0.0366
180	35.5	2.3	0.0528
135	42.5	1.7	0.0665
126	45.5	1.58	0.0695
110	47.5	1.4	0.111
88	53.0	1.1	0.131



## Discussion

When the relation between vapor-pressure lowering and concentration of the rubber jellies is compared with that of molecular disperse solutions, *e. g.*, paraffin oil in benzene, or sucrose in water (Berkeley and Hartley, *Proc. Roy. Soc.*, **77A**, 156 (1906)), a large difference is immediately noticeable. Up to a certain concentration the rubber causes no appreciable vapor-pressure lowering, but beyond this the lowering increases rapidly with concentration, whereas molecular disperse solutions give a linear relationship up to a concentration of 40–50%.

The agreement between the values obtained with different samples of rubber shows that they are of a very uniform nature and not mixtures of hydrocarbons of different degrees of polymerization, thus supporting Harries' views on the existence of a definite rubber hydrocarbon, which have recently been emphasized by Pummerer, Nielsen, and Gündel (*Ber.*, **60**, 2167 (1927)).

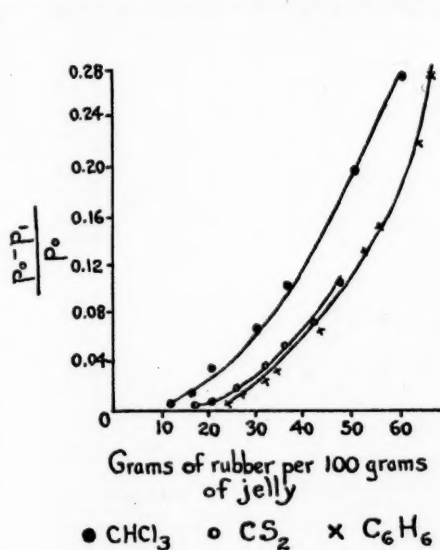


Figure 3

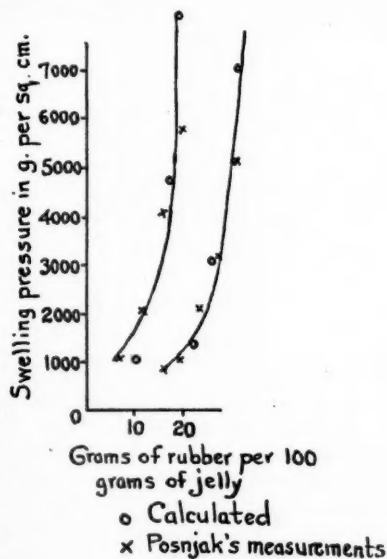


Figure 4

Over-masticated rubber, which combines with the solvent, giving a viscous liquid, behaves in exactly the same manner as the original untreated material, which in the swollen condition is an elastic solid. This behavior makes highly improbable the explanation of the swelling phenomena by assuming capillary forces (Freundlich and Posnjak, *loc. cit.*, p. 454; Kruyt, *Colloids*, p. 228), and supports Katz's theory, based on the similarity between the vapor-pressure isotherm of jellies and those of concentrated solutions, that swelling is mainly a process of solution. The present values obtained with much less concentrated solutions of rubber show that the behavior is different from that of a molecular disperse solution, Freundlich (*Kapillarchemie*, 2nd ed., p. 923) thinks that a similarity to a process of adsorption exists, with the difference that, whereas in the case of glass, for example, only the molecules on the surface are active, in the case of jellies all the molecules combine with the solvent. This explanation is similar to that given for the process of solution when the molecules of the solute are surrounded with a solvation layer, and would hold also in the case of the "liquid" jelly of over-masticated rubber. It

does not claim merely a surface adsorption or the presence of a solid wall. The incompleteness of theories explaining this part of the process of solution is discussed by Freundlich (*op. cit.*, p. 67). It seems very probable that the forces causing the imbibition of solvent in the jelly are similar.

On this basis it is possible to explain the shape of the isotherm given in Fig. 3. Only above a certain rubber concentration (about 10–20%) is appreciable vapor-pressure lowering observed: the solvent only loses its activity when it comes within the sphere of action of the molecules. The thickness of this solvated layer, in which the vapor-pressure lowering begins, can be calculated roughly. According to Sheppard, Nietz, and Keenan (*Ind. Eng. Chem.*, **21**, 126 (1929)), the thickness of the rubber molecule is 4–6 Å.U., which corresponds to two carbon atoms in the isoprene molecule. Assuming that the molecules are only long chains, the width will correspond to the thickness of one carbon atom, *i. e.*, approximately 2 Å.U. As a rough approximation, we will consider the molecules as rectangular prisms and neglect the distance between them. The total length of rubber molecules in a given volume, *e. g.*, 1 cc. when they are linked together in one long chain is equal to (volume)/(width × thickness), and from the above values this is  $0.125 \times 10^{16}$  cm. Further, if the thickness of the solvated layer is the same in both dimensions, for a given volume of solvent the thickness of this layer ( $x/2$ ) can be calculated from the formula  $(T + x)(W + x) = V/L$ , where  $T$  is the thickness of the molecule (4 Å.U.),  $L$  the length and  $V$  the volume of 1 cc. of rubber together with its solvated layer, and  $W$  its width (2 Å.U.). It is tacitly assumed that the solvated molecule has the same shape as the original molecule.

In the case of benzene,  $V$  is 5.25 cc. when  $(p_0 - p_1)p_0 = 0.0042$ , whence  $x/2$  is about 2.0 Å.U.; and for chloroform  $x/2 = 2.0$  Å.U., when  $(p_0 - p_1)/p_0 = 0.0034$  and  $V = 8$ . The thickness of the solvated layer as calculated from the smallest vapor-pressure lowerings is thus of the order of the radius of molecular attraction.

The values of swelling pressure calculated from the vapor-pressure lowering show a rough agreement with the values actually measured by Posnjak, but as his measurements were only over a very small range of concentration it is not possible to say how far the agreement will hold at higher swelling pressures.

In the case described above, it is possible to say that swelling is due to the attraction of the molecules of the jelly to those of the solvent. This results in a surrounding solvation layer. Solvent molecules show vapor-pressure lowering in this layer and naturally exhibit swelling pressure. This behavior is similar to (or identical with) that part of the process of solution in which the *solute becomes surrounded by a solvated layer*. The other part of the process of solution, in which van't Hoff's law holds, is different. It is remarkable that substances which show swelling are generally of high molecular weight and, according to recent investigations, long chains of unimolecular thickness (Sheppard and Keenan, *Nature*, **121**, 982 (1928); Knight and Stamberger, *J. Chem. Soc.*, **1928**, p. 2791; Katz and Samwell, *Naturwissenschaften*, **30**, 1513 (1928)). This behavior seems to be a special property of this class of substance.

That the solvation of jellies is a molecular process and not a micellar one is most probable, because reproducible values were obtained with different samples after different treatment, and approximately the same molecular concentration causes the same relative vapor-pressure depression.

The process of swelling can be sufficiently explained by assuming that the solid molecules of the jelly are surrounded by a solvated layer, and there is no reason to assume the existence of a solid solution of solvent in the jelly (Katz, *loc. cit.*). This would not hold in the case of liquid over-masticated rubber jellies.

### Summary

Methods and results of measurement of vapor-pressure lowering of rubber jellies are described.

From the qualitative behavior of the jellies (consistency), from the shape of the curve given in Fig. 3, and from approximate calculations of the thickness of the solvent layer round the molecules, it is assumed that the solvent is bound by the molecules of the jelly in the form of a solvated layer.

The existence of such a layer in the sphere of action of the molecules explains sufficiently a decrease of activity of solvents, which results in vapor-pressure lowering, swelling pressure, etc., and makes the process similar to that of solution.

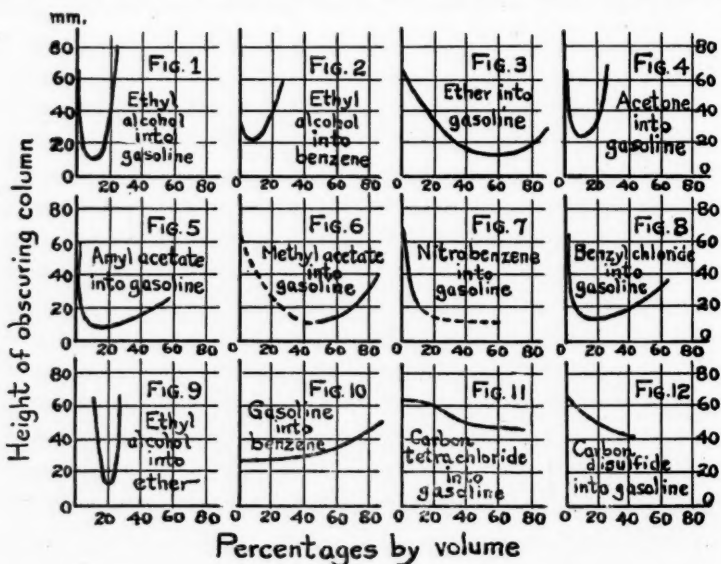
My best thanks are due to Professor F. G. Donnan, F. R. S., for valuable suggestions and criticism during this investigation.

# Studies of Conditions Affecting the Vulcanization of Rubber. III. Some Properties of Rubber against Solvents

Yutaka Toyabe and Kenji Fukunaga

FUJIKURA ELECTRIC WIRE CO., TOKIO

The authors have determined the solubility of unvulcanized compounded rubber containing 20 per cent. by volume of zinc oxide. The obsurometry method described in a previous report on various mixed solvents was used in the experiments.



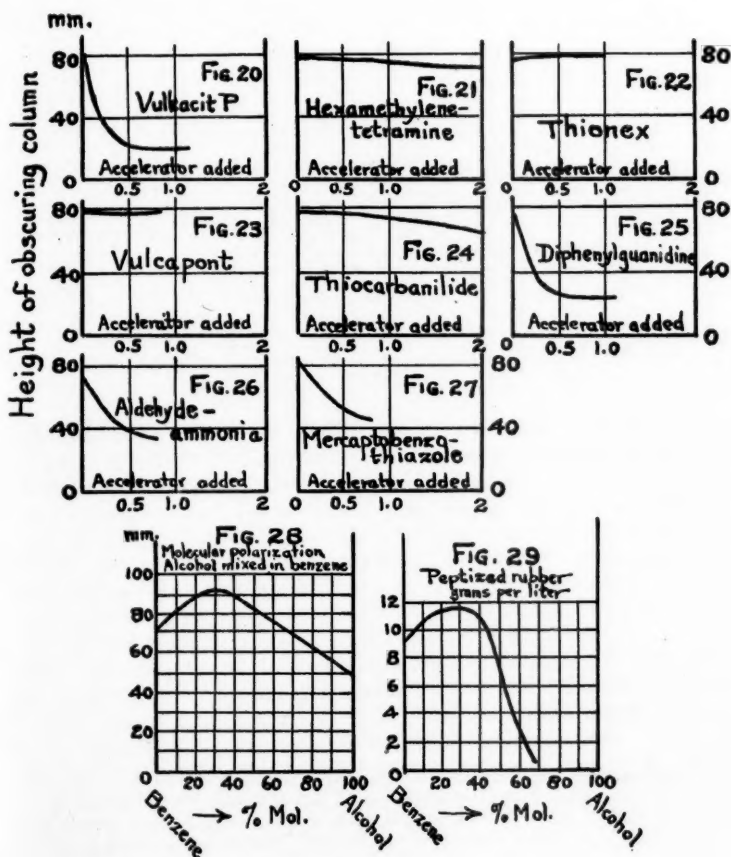
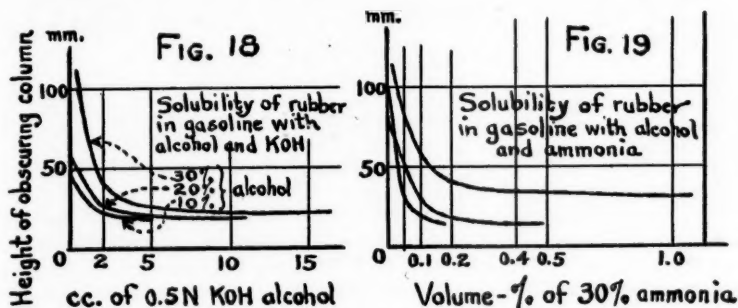
It was observed that the addition of a small quantity of certain solvents such as ethyl alcohol, acetone or nitrobenzene increases considerably the solvent power of the original solvents, such as benzene or gasoline. The results are shown in Figs. 1 to 12.

Similar effects were also observed when inorganic bases or organic accelerators were added to the solvent, as shown in Figs. 18 to 27. These phenomena may be explained by Whitby's electroviscous effects (cf. *Second Colloid Symposium Monograph*, 1925, pp. 16-28).

In the process of peptization of raw rubber in benzene-alcohol mixtures, the so-called gel-skeleton of rubber was easily dispersed in benzene with alcohol or an organic accelerator, whereas it was very difficult to disperse in benzene alone, and in the former case many sub-microns were observed under the ultra-microscope.

The authors suppose that the action of these added substances is similar to that of mastication as explained by Klein (cf. *Kolloid-Z.*, 25, 362(1924)) i. e., a breaking-down of the gel-skeleton of rubber and an increase in the number of sub-microns under the ultra-microscope.

The peptization of raw rubber in benzene-alcohol dehydrated with calcined cop-



per sulfate was also observed. It was found that the peptization maximum coincided with the maximum of molecular polarization of the mixed solvents given by Debye and Ostwald (cf. *Kolloid-Z.*, 45, 56 (1928)), lying at 33-35 mol. % of alcohol, as shown in Figs. 28 and 29.



# The Formation of Thin Films of Organic Colloids on Mercury Surfaces\*

R. L. Keenan\*\*

## Introduction

The investigation described forms part of a series of studies on molecular orientation in relation to colloid structure which are being carried out in these laboratories. One object is to develop quantitatively a hypothesis proposed by Sheppard<sup>1</sup> concerning so-called emulsoid colloids, also termed "high molecular" substances. A preliminary note on the present work was communicated to *Nature*.<sup>2</sup>

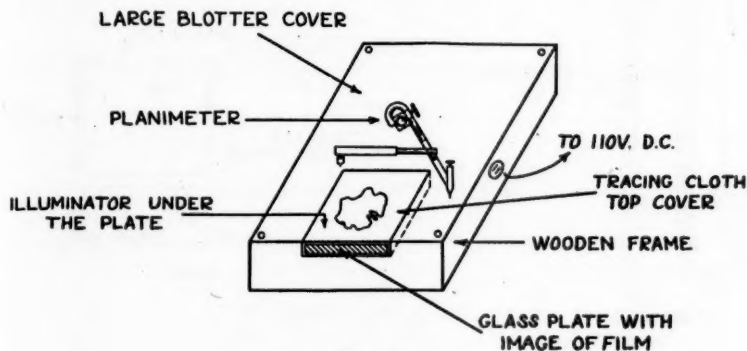


Figure 1

Studies of "high molecular" bodies, such as cellulose, rubber, and proteins have been made from various angles, *i. e.*, viscosity, X-ray crystal structure, molecular weight, polarized light, and chemical reactions. Each of these methods has given interesting pictures of these supposed large molecules. There is, however, one property of materials which has given extraordinarily vivid pictures of the sizes and shapes of many long chain compounds, such as the fatty acids and their esters. It was thought that this property, the spreading of materials on liquid surfaces, might be of use in the study of organic colloids.

Langmuir<sup>3</sup> showed that when films of fatty acids were extended to their limit, the molecules were oriented so that their carboxyl groups were in the water and the hydrocarbon group extended up from the surface. Knowing the weight of material, its density, and the area it covers, the thickness of the films, or in other words, one dimension of the molecule could be determined.

\* Read at the Swampscott meeting of the Am. Chem. Soc., Colloid Division, Sept., 1928.

\*\* Communication No. 363 from the Kodak Research Laboratories.

<sup>1</sup> The Nature of the Emulsoid Colloid State, *Nature*, **107**, 73 (1921).

<sup>2</sup> Sheppard and Keenan, *Nature*, **1928**, 982.

<sup>3</sup> Langmuir, *J. Am. Chem. Soc.*, **39**, 1869 (1917).

If solutions of these polymers could be spread on a suitable support, there was a possibility of measuring at least one dimension of the molecule.

### Previous Work

Dewhurst<sup>1</sup> wishing to obtain as thin a film as possible for his rapid volometer was successful in getting collodion films from ether-alcohol solutions by allowing them to spread on a clean mercury surface. These films were many molecules thick and useless for our purpose.

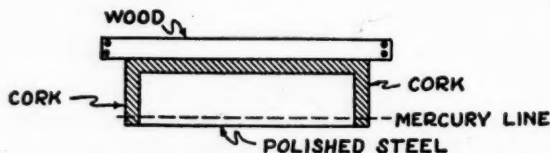


Figure 2—Scraper

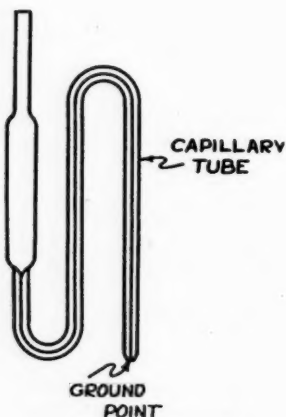


Figure 3—Dropper

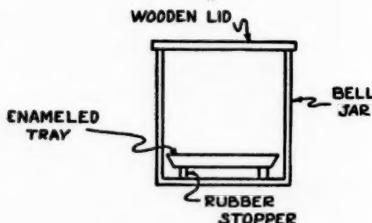


Figure 4

Barton and Hunt<sup>2</sup> obtained colloidal films 10 to 20 Å.U. thick by allowing amyl-acetate solutions to spread on a clean water surface.

Fischer<sup>3</sup> spread certain oils on mercury and determined their thicknesses by the volume-area method. The outline of the film was determined by breathing upon the mercury surface. His results were in agreement with Langmuir's and Adams'.

Wallbott<sup>4</sup> spread collodion, gelatin, and other such films on mercury for the purpose of studying phase shifts of light by reflection. His films were relatively thick.

Taylor<sup>5</sup> was successful in making celluloid films on mercury from 30 to 700 Å.U. thick for a vacuum-tight membrane. Celluloid spread on water did not give vacuum-tight membranes which was possibly due to an orientation effect. This effect was more or less absent when the celluloid was spread on mercury.

<sup>1</sup> Dewhurst, *Proc. Phys. Soc.*, **39**, 39 (1926).

<sup>2</sup> Barton and Hunt, *Nature*, **114**, 361 (1924).

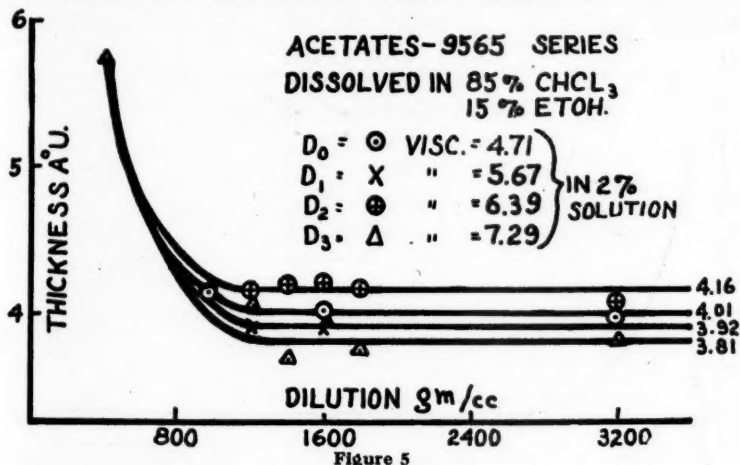
<sup>3</sup> Fischer, *Ann. Physik*, **68**, 414 (1899).

<sup>4</sup> Wallbott, *Ann. Physik*, **68**, 496 (1899).

<sup>5</sup> Taylor, *J. Sci. Instr.*, **3**, 400 (1926).

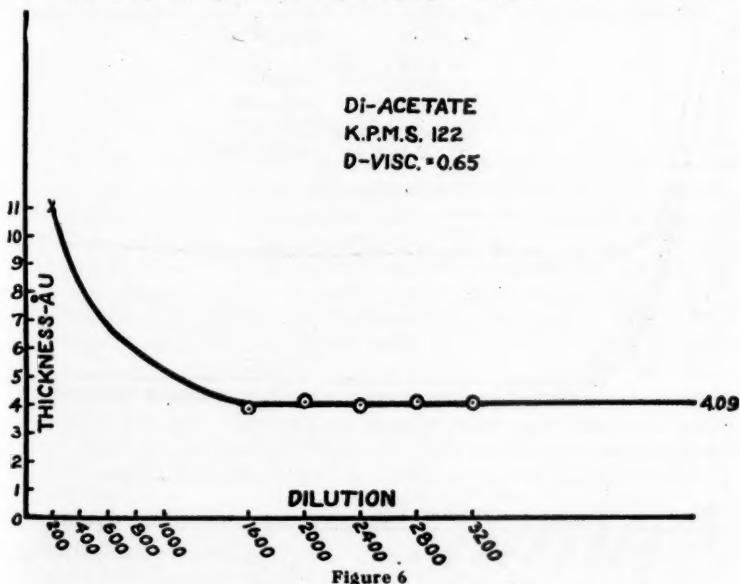
## Preliminary Work

Observations on the behavior of these films on water indicated that water was not the ideal substance on which to do the work. Many of the best solvents for cellulose esters are soluble in water or are denser than water and tend to drag the cellulose esters below the surface. Consequently mercury was chosen. For some time, however, it appeared to be equally unsatisfactory.



## Purification of the Mercury

The mercury was electrolyzed for three days by making it a cathode in a weak nitric acid solution. It was washed free from acid, dried, and distilled three times in a vacuum, then placed in a photographic tray and covered with a thick



film of cellulose acetate which was scraped off after some hours. It was found that the mercury improved steadily for several weeks after fresh films were coated on it and scraped off. At first, the films could not be formed by spreading but, as the surface became purer, spreading was finally accomplished. A thin film was always left on the surface when not in use. Thus a clean surface could easily be obtained by the scraping procedure.

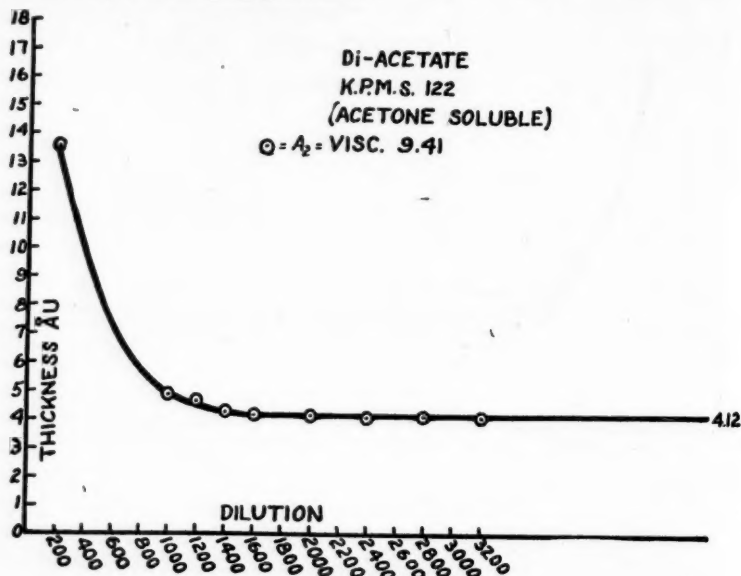


Figure 7

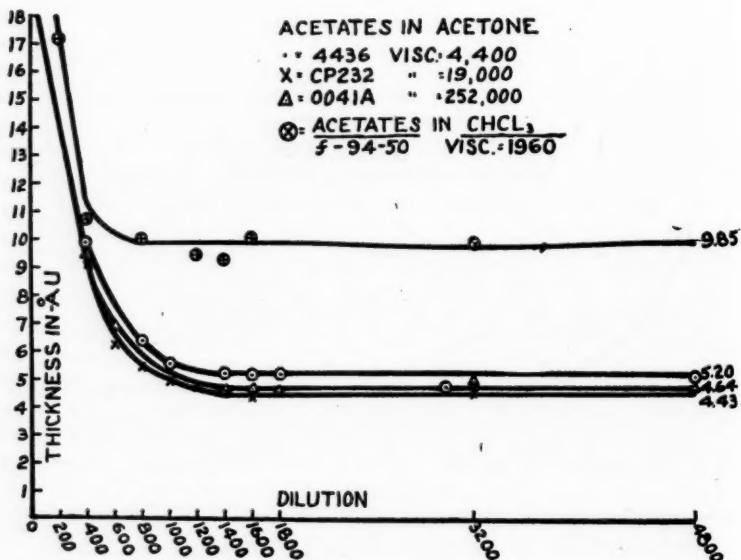


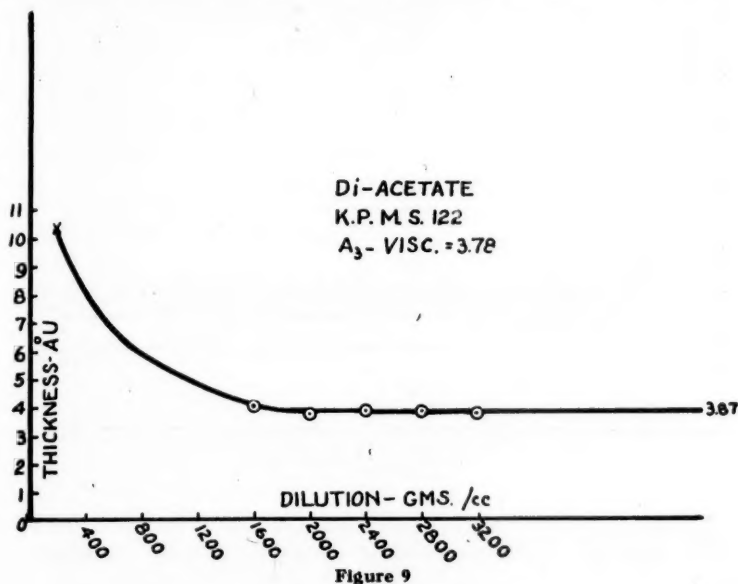
Figure 8

## Materials

The cellulose nitrates and acetates in the best state of purity were obtained in these laboratories. Solutions were made from solvents prepared at the Synthetic Organic Chemicals Department of the Eastman Kodak Co. and were of their purest stock.

The rubber was prepared by extracting pale crepe with acetone to remove resins, and then diffusing it through a silk bolting cloth bag into petroleum ether, according to Feuchter's method.

The iso-electric gelatin was prepared by Hudson of these laboratories.



## Description of the Apparatus

The apparatus consisted of an enameled photographic tray 4 cm. deep, 20 cm. wide, and 30 cm. long, which was placed in a bell jar fitted with a wooden cover to protect the mercury surface from air currents and to keep dust from settling on the mercury while standing overnight (Fig. 4).

A scraper of flexible steel (Fig. 2) was made to fit tightly into the photographic tray by having strips of sheet cork at the ends. This scraper was allowed to dip a short distance into the surface of the mercury, which made it possible to scrape all surface impurities to one end of the tray.

The material was deposited on the mercury surface from a standardized dropper with a ground tip (Fig. 3). Only one drop of solution could be used for a given film. Drops falling after the first one do not touch the mercury surface but, instead, fall upon the solid film formed by the first drop, thereby preventing spreading. This was found to be true for those substances forming rigid (condensed) films.

A planimeter was used to measure the area of the film of which an outline had been traced on a glass plate (Fig. 1). The rigidity and irregularity of the film made direct area measurements impossible.

## Experimental Procedure

A drop of solution containing a known amount of material was allowed to fall upon the scraped mercury. A film was obtained within a fraction of a second. The image of the film, developed with talc, was traced on a glass plate laid over the tray, and its area measured with a planimeter (Fig. 1). Several area measurements were made at each concentration (dilution). The dilutions were carried

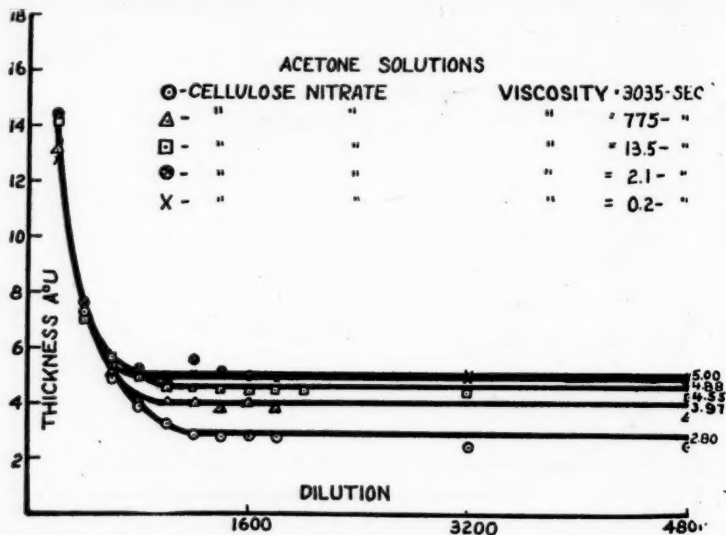


Figure 10

out to the point where the independent relation between thickness and dilution was well established. Solvent correction was made in each case where it was necessary.

In order to standardize the technique for working on mercury, several of the fatty acids were spread on mercury and the results compared with those recorded in the literature. These may be seen in Table I.

TABLE I

Compound	Formula	Solvent	T.Å.U.	T.Å.U.	Observers
Elaidic acid (isomer of oleic)	$C_{17}H_{33}COOH$	Ether	12.2	11.2 (oleic)	Langmuir
Stearic acid	$C_{17}H_{35}COOH$	Ether	21.9	21.8-25.0	Langmuir
Myristic acid	$C_{13}H_{27}COOH$	Acetone	22.5	21.1	Adams
n-Capric acid	$C_9H_{19}COOH$	Ether	13.6		

## Discussion of Results

Figures 5 to 10 show clearly that definite limit films of these bodies can be obtained on mercury. In the case of the cellulose esters and gelatin, an irregular solid film was obtained (Fig. 11). At first, one might think that a drop of solution should spread in a circular fashion on a clean surface, but this is not the case.

When a drop of solution falls on mercury the surface forces cause spreading. The edge of the drop becomes thin, as it is forced out along the surface from the center, and the solvent evaporates, leaving a solid film of cellulose ester surround-



ing an island of solution. The surface forces continue to be effective, causing a squeezing out of more material from the center of the drop in order to reach its limit of spreading (monomolecular layer). To spread further, this solid film at the edge must break and let more solution out, pushing the thin solid rim to the side.

This causes a very irregular-shaped film, characteristic of the rigid films of this type.

Table II gives the comparative spreading and thickness relations between the cellulose esters at varying viscosities. The concentration 1 to 1600 was taken because all of the limit films could be noticed there as well as at higher dilutions and the 1 to 1600 concentration was more representative. The viscosities in column two are comparable in each series but not from one series to the next.

In the case of the nitrates an inverse relation between thickness and viscosity was found (Fig. 10).

A paper on "The Supramolecular State of Polymerized Substances in Relation to Thin Film and Interfaces"<sup>1</sup> contains a theoretical discussion on these thin films, from which the following conclusions are extracted.

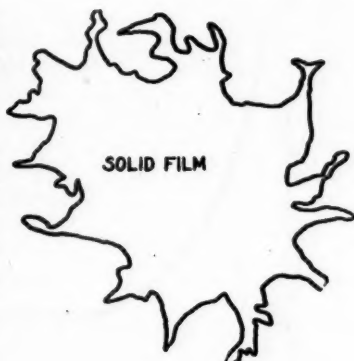


Figure 11

TABLE II  
COMPARISON DATA

Cellulose Acetate Substance	Viscosity Centipoises	Concen- tration	Area Sq. Cm. $\times 10^{-3}$ Cm.	Thickness	Remarks
F-94-50	1960	1-1600	53	9.85	CHCl <sub>3</sub> soluble tri- acetate
C.P. 232	19,000	1-1600	241	4.43	Comb acetates Acetone soluble*
0041A	252,000	1-1600	230	4.64	
4436	4,400	1-1600	206	5.20	
9565D <sub>0</sub>	4.71	1-1600	142	4.01	85% CHCl <sub>3</sub> } soluble 15% EtOH } Hydrolyzed in suspen- sion*
9565D <sub>1</sub>	5.67	1-1600	146	3.92	
9565D <sub>2</sub>	6.39	1-1600	135	4.16	
9565D <sub>3</sub>	7.29	1-1600	145	3.81	
M.S. 122A <sub>2</sub>	9.41	1-1600	257	4.12	Di-acetates Acetone soluble
M.S. 122D	0.65	1-1600	273	4.09	
M.S. 122A <sub>3</sub>	3.78	1-1600	262	3.87	
Cellulose Nitrate	Viscosity Seconds				
T 59	3025	1-1600	296	2.80	Acetone soluble
T 321	0.20	1-1600	168	5.00	
T 65	775	1-1600	202	3.97	
T 64	13.5	1-1600	186	4.55	
T 322	2.10	1-1600	170	4.88	

\* Approaching the di-acetates on acetyl contact.

<sup>1</sup> Sheppard, Nietz, and Keenan, *Ind. Eng. Chem.*, **21**, 126, 1929.

These strikingly thin films seem to support the theory<sup>1</sup> that the cellulose bodies are composed of ribbons or chains of  $C_6H_{10}O_5$  groups of an indefinite length, and a thickness amounting to approximately 2.5 Å.U. to 4.5 Å.U.

The iso-electric gelatin spread from water solutions on mercury (Fig. 12) gave

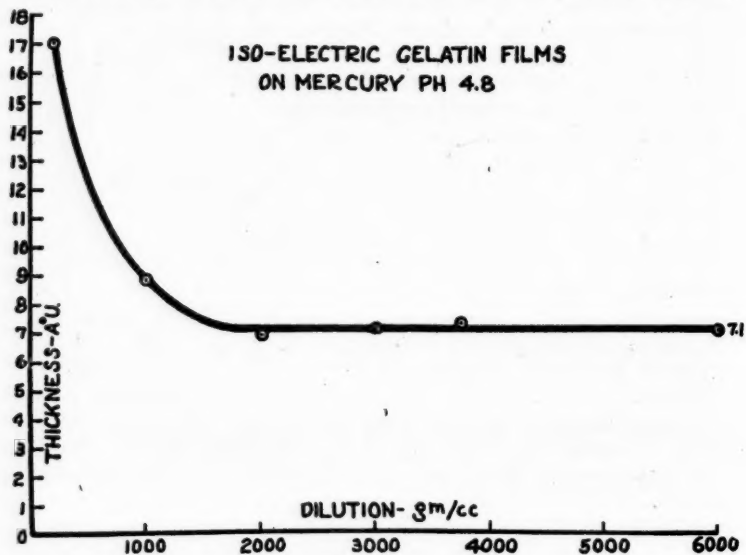


Figure 12

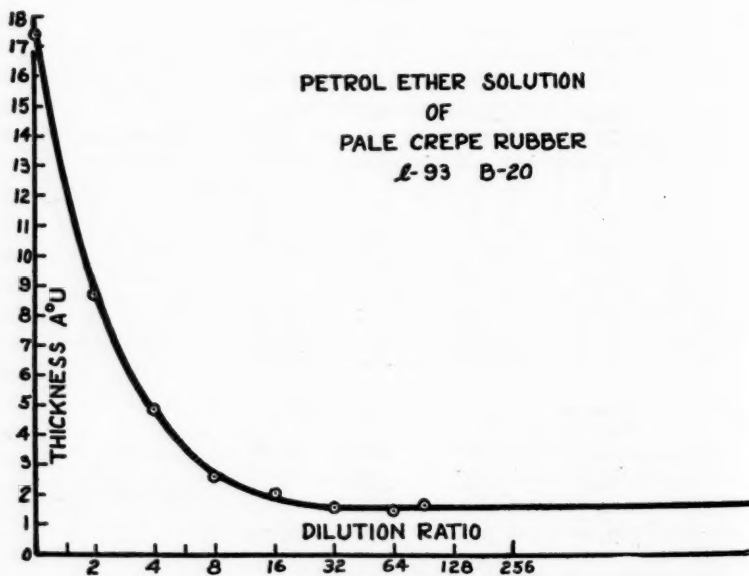


Figure 13

<sup>1</sup> Sponsler and Dore, *Fourth Colloid Symposium Monograph*, 174-202 (1925).

values in good accord with the values obtained by Gortner and Grendel<sup>1</sup> for protein films on water.

The thinnest films obtained on mercury were those of rubber (Fig. 13). The thickness value (1.5 Å.U.) may possibly represent the value for the methyl group in Staudinger's isoprene chain.

Recently, Devaux<sup>2</sup> has described his work on the formation of thin films of sugars, starch, and albumen on mercury. His values also show extraordinarily thin films but his conclusions seem hardly necessary in view of the similarity between certain films formed on aqueous solutions and non-aqueous solutions.

If these films cannot be considered as a measure of one dimension of the molecule, then we must believe that they are not continuous, but consist essentially of a network structure. Work bearing on this phase is being started and it is hoped that the porosity, if it exists, may be determined.

### Summary

1. A technique has been developed for obtaining thin films of organic colloids on mercury.
2. Several series of cellulose acetates, with varying viscosities and indifferent solvents, were used.
3. In the case of the cellulose nitrates, the limit film thickness varied in an inverse relation with the viscosity of the solutions.
4. Films of rubber and iso-electric gelatin were formed on mercury.
5. Films of the cellulose esters and gelatin were rigid, and condensed, while the rubber films were elastic.
6. The limit thickness increased with increasing complexity of the atom groups as:

Rubber  
(C, H)  
1.5 Å.U.

Cellulose  
(C, H, O)  
2.5 to 5.0 Å.U.

Gelatin  
(C, H, O, N)  
7.0 Å.U.

### Conclusion

The results indicate that these films are composed of long chains or ribbon-like molecules lying flat upon the surface or of an open-work structure somewhat like a fish net.

The author wishes to express his appreciation for the valuable suggestions given by S. E. Sheppard and E. K. Carver of these laboratories.

<sup>1</sup> Gortner and Grendel, *Trans. Faraday Soc.*, **22**, 477 (1926).

<sup>2</sup> Devaux, *J. Phys. Radium*, **9**, 345 (1928). See also Sheppard and Keenan, *Nature*, June 23, 1928.

# The Natural Coagulation of *Hevea* Latex

Alexander Steven Corbet

It is well known that if an incision be made in the bark of *Hevea brasiliensis*, a viscous, creamy white liquid latex exudes. In the course of a few hours after tapping, the latex begins to clot and eventually a solid mass of rubber is formed and floats on the surface of a serum, which may be clear or of a milky color.

The agencies by which the changes occurring during natural coagulation are promoted have been the subject of many investigations during the last two decades. Although progress was slow at the outset, rapid strides have been made in recent years and we appear to be in sight of a solution of the problem.

Formerly, two different lines were taken in explaining the phenomena and a not inconsiderable amount of evidence, although largely circumstantial, was adduced in support of the rival hypotheses. One body of workers considered natural coagulation to be the work of enzymes, while the other attributed it to bacterial activity. It is noteworthy that the supporters of enzyme action have had to shift their ground on more than one occasion. Later workers have shown fuller appreciation of the complexity of the subject and have displayed some reluctance in attempting an explanation of the subject in terms of any one theory.

## The Enzyme Theory

Although Spence<sup>1,2</sup> announced the presence of an oxidizing enzyme in *Hevea* latex over twenty years ago, it was in 1912 that Whitby<sup>4</sup> came to the conclusion that the natural coagulation of latex was due to enzyme activity. This view received the support of Campbell,<sup>7</sup> as a result of work on the relation between calcium salts and coagulation, and of Barrowcliff,<sup>9</sup> who discovered that coagulation proceeded in the presence of bactericides, such as chloroform, but was inhibited by hydrocyanic acid, a substance known to be toxic to both bacteria and enzymes.

More recently de Vries and his co-workers<sup>15,16,18,20,21,22</sup> have carried out extensive researches on the subject and consider that, while bacteria play a part in initiating the process, coagulation is finally affected by a specific enzyme, coagulase, which is present in *Hevea* latex.

Much of the evidence adduced in support of an enzyme theory of coagulation has not borne closer scrutiny. To take one instance, chloroform, toluene, and thymol are now known to be without toxic action on latex bacteria.

The outstanding points in favor of this theory which have not yet been completely explained on other grounds are listed below:

(I) Latex which has been sterilized (the enzyme presumably destroyed) does not coagulate on standing or in presence of acid, but does so after addition of a small quantity of fresh latex.\*

(II) Coagulation is accelerated by addition of calcium salts, which are known to favor clotting enzymes, but inhibited by calcium precipitants such as oxalate and fluoride.†

\* This statement, first made by Barrowcliff, appears, in general, to be true although Eaton and Grantham<sup>8</sup> and Belgrave<sup>19</sup> have refuted it. Van Harpen<sup>23</sup> now offers another explanation.

† Belgrave<sup>19</sup> has weakened the case for the enzyme theory by pointing out that sulfate (not a calcium precipitant) also inhibits coagulation.

(III) Campbell<sup>7</sup> and Whitby<sup>10</sup> have pointed out the analogy existing between latex coagulation and the clotting of blood and of milk, respectively.

### The Bacterial Theory

The first attempt to explain the coagulation of *Hevea* latex on a bacteriological basis was made by Eaton and Grantham.<sup>5</sup> These investigators launched certain criticisms at the enzyme theory and, as a result of their researches, concluded that natural coagulation is due to the activity of certain bacteria which infect the latex after collection.

The views of Eaton and Grantham received considerable support from the work of Gorter and Swart,<sup>6</sup> who found lactic acid present in the serum after latex had been coagulated in presence of sugar. Gorter and Swart considered that lactic acid was a result of the presence of fermenting organisms, and other organisms were responsible for the putrefactive changes occurring at the surface of the medium.

A bacteriological study of *Hevea* latex was carried out by Dernier and Vernet<sup>8</sup> and their results are of considerable interest. Although twenty-seven different bacteria were isolated by these workers only one of them, *Bacillus No. 1*, was present in all samples examined. *Bacillus No. 1* was distinctive also in being the only organism found which was able to ferment "dambosite"—the latex "carbohydrate."

At a later date, Belgrave<sup>13</sup> summarized the situation and gave further experimental evidence in favor of the bacterial theory.

The points in favor of the bacterial theory are:

(I) Latex collected under sterile conditions remains liquid and latex sterilized by heat does not undergo coagulation until exposed to fresh infection.

(II) In his attempts at collecting sterile latex, Belgrave found bacteria present in latex which coagulated, but none in latex which remained liquid.

(III) Of the bacteria found in latex, one species fermented the latex "carbohydrate" with production of acid and this bacillus was present in all samples examined.

### The Work of de Vries and Beumée-Nieuwland

De Vries and Beumée-Nieuwland consider,\* that the stability of latex is dependent on two factors, (I) the electric charges on the rubber particles and (II) solvation.

Rubber in latex is a negatively charged colloid and has a low degree of solvation. Consequently flocculation of the particles can be brought about either by neutralizing the charges with positively charged ions or by the agency of a dehydrating agent such as alcohol. It is well known, of course, that addition of acid or alcohol to latex results in coagulation, but alcohol is not able to effect precipitation of the hydrocarbon particles after the serum salts have been removed by dialysis.

Under ordinary conditions separation of the rubber particles may occur by (I) creaming, a purely mechanical and reversible change due to the action of gravity; (II) flocculation, in which the separated rubber particles do not adhere and can be temporarily redispersed by shaking. Flocculation is brought about by addition to latex of an electrolyte which causes unloading of the charges to such an extent that the mutual repulsion of the now feebly charged particles is more than counter-balanced by the molecular attraction existing between them; (III) coagulation, the stage following flocculation and in which the flocculi unite to form a coherent clot.

Natural coagulation is the result of bacterial activity. The latex bacteria attack certain carbohydrate-like compounds present, acids are produced and the  $p_H$  value of the medium is lowered. When the  $p_H$  value has dropped to about 5.0,

\* See Kruyt and de Jong, *Z. phys. Chem.*, **100**, 250 (1922).

flocculation of the rubber particles occurs and the process of coagulation is completed by the enzyme, coagulase.

Latex containing the bacteria and no enzyme (sterilized latex inoculated with bacteria) can reach only the flocculation stage; while latex containing only the enzyme (latex collected from the tree under sterile conditions) undergoes neither flocculation nor coagulation. Latex in which the enzyme alone is present, however, retains the power to coagulate latex which has already reached the flocculation stage.

The ability of acids to produce coagulation in latex is affected by heating, the more dilute the latex solution the higher the temperature to which it must be raised before this power is destroyed. After a 10 per cent. solution of latex has been heated to 75° C. for a few minutes, it can no longer be coagulated by addition of acid but, with a 33.3 per cent. solution, the same result is attained by heating to 65° C. Thus, inoculation of B. mixture\* with bacteria results in flocculation and not coagulation, although the rubber particles may eventually cohere mechanically; acetic acid also can produce only flocculation and not coagulation.

De Vries and Beumée-Nieuwland point out that the so-called "acid gap"\*\*\* in latex is simply an example of the phenomenon of irregular series, well known with other colloids systems,† and is due to the discharge of the charges on the colloid particles by electrolytes and reloading with charges of the opposite sign. Enzymes do not necessarily play any part in it.

As emphasized by de Vries and Beumée-Nieuwland, latex containing neither enzymes nor bacteria is probably changed latex.

#### The Present Investigation

Samples of latex of various ages were examined and, in all cases where coagulation had begun, the samples were found to be swarming with bacteria. Cultures of organisms were prepared and a bacillus was isolated without difficulty. This organism was the predominant feature of the latex flora and was invariably present in all samples examined from the States of Selangor, Perak, and Johore.

The bacillus has been studied in considerable detail and appears to be responsible for most of the important biochemical changes which occur in latex during natural coagulation. It does not appear to have been denominated previously and the name *Bacillus pandora* is proposed for it.

Cultures were prepared on glucose-agar slopes and sub-cultures were made at weekly intervals. The characterization of the organism is given in detail later, but some of the characters and reactions are of particular interest.

The organism is rather large and, as it stains readily with carbol-fuchsin,‡ there is little difficulty in identifying it in mixed cultures. It is motile and the flagella admit of staining by Loeffler's method. It is gram-positive, contrary to the statement of Dernier and Vernet, who found their *Bacillus No. 1* to be gram-negative. *B. pandora* is a spore former and a facultative anaerobe§ and, in consequence of the latter characteristic, is able to effect chemical changes both in the liquid and at the surface.

\* Ten per cent. latex solution maintained at boiling temperature for a few minutes.

\*\* While addition of acid to latex results in coagulation, the initial addition of a greater quantity may not cause precipitation; further addition of acid, however, will again result in coagulation. Van Harpen has recently determined the  $pH$  values of latex at which these changes occur.

† See, for example, the flocculation of a platinum sol by ferric chloride. (Buxton and Teague, *Z. phys. Chem.*, **57**, 72, 79 (1904).)

‡ See Belgrave, *Malayan Agr. J.*, **11**, 351 (1923).

§ B. J. Eaton informs me that Stanton, formerly Bacteriologist and later Director at the Institute of Medical Research, Kuala Lumpur, isolated an organism from *Hevea* latex which proved to be a facultative anaerobe. The work has not been published.



Gelatin is liquified by *B. pandora*, nitrates are reduced, and litmus is rapidly decolorized. Acid formation occurs in the presence of sugars and of milk but only in the case of lactose and sucrose has gas evolution also been observed.

Chain formation was not marked but appears to be more noticeable in older cultures. The cultural features were not distinctive, the colonies on both agar and glucose being punctiform. Tests for the production of hydrogen sulfide gave negative results.

Inoculation of solutions of latex and latex products with *B. pandora* gave interesting results.

Addition of the organism to sterile 10, 20, and 33.3 per cent. aqueous solutions of latex produced flocculation in 2 or 3 days. In some instances, coagulation was observed after two or three weeks, but the tendency toward formation of a coherent clot varied from sample to sample. It can be stated, however, that coalescence is favored by a high concentration of latex in the solution. Acidification without gas evolution resulted from inoculation of latex serum and of a solution of the so-called latex "carbohydrate," (methyl-*l*-inositol) prepared from latex by extraction with alcohol.

Experiments showed that the  $p_H$  range of *B. pandora* is wide, the organism being detected in solutions whose  $p_H$  values ranged between 4.2 and, 10.2. Ammonia *per se* does not appear to have any toxic properties whatever and sodium sulfite, in the concentration in which it is usually employed as an anti-coagulant, is also without bactericidal action.

It seems highly probable that the *Bacillus* No. 1 of Dernier and Vernet is identical with *B. pandora*, and a comparison of characters is given below.

	<i>Bacillus</i> No. 1	<i>B. pandora</i>
Latex coagulation	...	+
Acidification of "dambose"	...	+
Acidification of lactose	...	+
Acidification of sucrose	...	+
Coagulation of milk	...	+
Albumen digestion	...	+
Gelatin liquefaction	...	+
Gram stain	...	+
Motility	...	+

It will be seen that the experimental results wholly support the bacterial theory of natural coagulation, and the mechanism by which the stage of flocculation is reached is in accord with the views of de Vries and Beumée-Nieuwland.

Latex, as it issues from the tree, is almost certainly free from bacteria, for latex removed from the tree under sterile conditions remains liquid.

The fact that *B. pandora* is a spore-former indicates that it is to be found as spores on the tree trunk and enters the latex as it issues from the tapping cut. On a wet morning, the tree trunks are moist and, under such favorable conditions, the spores germinate. Thus, in addition to contamination at the tapping cut, active organisms will be carried to the latex flow by the rain running down the trunk. It would be anticipated that latex would coagulate more rapidly on wet mornings and such is known to be the case.

When the bacilli reach the latex, the carbohydrate substances are attacked and acids are produced.

Carbohydrates are always attacked in preference to other substances, as was realized clearly by Eaton and Grantham, for they showed that natural coagulation is accelerated by the addition of sugars to latex. The matter has also been discussed by Whitby.<sup>11</sup> Decomposition of the proteins sets in only when most of

the carbohydrate substances have been removed. When the latex has attained a definite degree of acidity (a  $p_H$  value of about 4.8 according to van Harpen) flocculation and coagulation of the rubber particles take place.

At this stage the rubber particles with adhering protein float to the top of the liquid and other changes begin. Possibly the organisms in the serum are now being killed by the acid they have themselves produced and only those at the surface can survive; but, in any case, the separated rubber has carried bacteria with it to the surface and there decomposition of the adhering proteins sets in. As a result, ammonia and probably other reduction products appear and the surface layer becomes alkaline. Hence, in coagulated latex, the liquid and the surface clot are found to be acid and alkaline, respectively. Both acid and alkali production can take place of course, in the liquid or at the surface, provided the necessary carbohydrate or protein substances are present.

Whether rubber particles in a state of flocculation are coagulated by an enzyme or a resinous substance is a matter beyond the scope of this paper.

In none of the experiments carried out was the surface scum evil-smelling or badly discolored and it does not appear likely that these results are produced by *B. pandora*.

### The Preservation of Latex

Substances in use at present as latex preservatives fall into two categories: (a) those employed to delay coagulation in the latex cups, known as "anti-coagulants;" (b) those used to preserve latex in the liquid state for an indefinite period during export, known as "preservatives."

All that is required of substances in the first class is that they delay bacterial activity for a few hours; it is not necessary that all organisms present should be destroyed. In Malaya, sodium sulfite is generally employed for this purpose and, for estate practice, Eaton\* recommends the use of a solution which gives 0.05 g.  $\text{Na}_2\text{SO}_3$  per 100 cc. latex. In the present investigation it was found that *B. pandora* was able to multiply in solutions containing four times this quantity of sodium sulfite.

The success of sodium sulfite as an anti-coagulant is to be attributed to the fact that dilute solutions of lactic acid are able to decompose sulfite with evolution of sulfur dioxide and formation of sodium lactate. In this manner, accumulation of acid in the latex is avoided and coagulation cannot take place until all the sulfite present has been decomposed. The anti-coagulant action of sodium carbonate admits of an explanation along similar lines.

It may be pointed out that, with the quantities of sodium sulfite usually employed on rubber estates, the concentration of sulfur dioxide is not sufficiently high for this compound to have a marked toxic action on the bacteria present. Its effect, if any, in this direction is very slight.

Formalin also has been employed as an anti-coagulant, probably on account of its well-known germicidal properties but, as its presence in excess has detrimental effects on the rubber, its use has been discontinued.

Ammonia in dilute solution has met with a measure of success as an anti-coagulant and its action is obviously to neutralize the acids as they are formed so that the  $p_H$  value of the latex does not reach that at which coagulation takes place.

As a preservative during export the use of ammonia is general, although in the present investigation it has been found that ammonia is without toxic properties as far as *B. pandora* is concerned. Of course, if the ammonia added is sufficient to

\* Rubber Research Institute of Malaya, *Planting Manual*, No. 1 (1928), on page 3, line 35, "5 fluid oz." should read "10 fluid oz."

raise the  $p_H$  of the latex to a value outside of the range of the organism, the bacterial activity will be destroyed; but this effect would be produced by any other strong alkali.

In actual practice, the quantity of ammonia added is not sufficient to raise the  $p_H$  value to the required figure, hence the microorganisms are not destroyed.

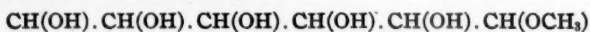
Eaton<sup>12</sup> recommends the use of 7 grams of ammonia ( $NH_3$  by weight) per liter of latex for preservation for shipment while de Vries<sup>14</sup> considers 5 grams per liter to be the minimum for good preservation. The presence of four times the latter quantity, however, will not ensure the complete absence of microorganisms. De Vries has shown that ammoniated latex exhibits a decrease in alkalinity on keeping although, in 0.25–0.3 per cent. solutions, the diminution is so slow that the latices keep well for over a year.

The action of ammonia as a preservative admits of an explanation as follows. The carbohydrate substances in latex are decomposed by bacterial action, with production of organic acids, which, however, are neutralized by the ammonia as soon as they are formed. After decomposition of the whole of the acid convertible substances, the proteins are attacked and ammonia production becomes the predominant action. During this stage there is a loss of ammonia by evaporation and a gain by bacterial activity but, when the protein is decomposed, the ammonia concentration remains constant, except for the losses by evaporation, while the bacteria may die from starvation or attack the lactates, etc., formed. It will be clear that if the initial concentration of ammonia is not sufficient to neutralize the acids formed, then coagulation will ensue eventually.

With the information available at present, it is not possible to evaluate accurately the acids produced by bacterial action but a calculation has been made which throws some light on the subject.

According to Pickles and Whitfield,<sup>3</sup> smoked rubber may contain as much as 2.5 per cent. methyl-*l*-inositol. Assuming a latex with a dry rubber content of 33.3 per cent., the methyl-*l*-inositol present will not exceed 0.8\* per cent.

Methyl-*l*-inositol has the structure



so that one molecule can give rise to five carboxyl groups. This value for acid production is almost certainly too high but can be regarded as the maximum.

On this basis, 0.8 g. methyl-*l*-inositol is equivalent to 0.93 g. (COOH) which, in turn, requires 0.35 g. ammonia for neutralization.

To be on the safe side, therefore, for preservation of latex for long periods, the initial concentration of ammonia should probably not be appreciably less than 0.35 per cent.

A consideration of the figures obtained by de Vries for the decrease of alkalinity exhibited by ammoniated latex indicates that the foregoing explanation is probably correct but the value given above for safe preservation may be slightly high.

A similar calculation for the mutual decomposition of sodium sulfite and lactic acid shows that for the complete preservation of latex by sodium sulfite, this salt must be present in amount exceeding 0.26 per cent.

Denier and Vernet have drawn attention to the toxicity of zinc salts to *Hevea* latex bacteria, and a few experiments were carried out to test this point. No *B. pandora* were found in solutions containing 0.06 per cent. zinc sulfate ( $ZnSO_4 \cdot 7H_2O$ ) growth was very poor in a 0.03 per cent. solution, while the organisms grew well in a 0.016 per cent. solution. When solutions of latex containing zinc sulfate

\* This value is in keeping with values given by Luff (*Chemistry of Rubber*, E. Benn, Ltd., London, 1923, p. 23) for the acetone-soluble substances present, viz., 1.22–1.65 per cent.

were prepared and inoculated with *B. pandora* the results were different, for coagulation occurred in a latex containing 0.12 per cent. of the zinc salt. The explanation of this discrepancy is probably to be found in the presence of phosphates in the latex. Addition of a zinc salt to latex will result in the precipitation of a zinc phosphate and, if the orthophosphate,  $Zn_3(PO_4)_2$ , is formed, about 0.64 g. of zinc sulfate will have to be added to 100 cc. of latex to ensure a solution containing 0.033 per cent. of the zinc salt.\*

### Experimental

*Isolation of Bacillus Pandora.*—Pure cultures of this organism were readily obtained, by the usual "plating-out" method, from latex about 2 days old. Glucose-agar was found to be a very suitable culture medium and was used throughout the investigation. When a pure culture had been obtained, sub-cultures were prepared weekly on glucose-agar slopes. A strain of *B. pandora* isolated in January was still maintaining a healthy and vigorous growth in August of the same year.

When the organism was required in any quantity, it was grown on a glucose-agar surface in a Roux bottle. After four or five days, sterile water was washed over the surface of the agar and a strong suspension of the organisms obtained.

The glucose-agar medium was that used by Millard and Burr† for work on *Actinomyces* and was prepared from the following formula:

$K_2HPO_4$	... 1.0 g.	$FeSO_4$	... 0.01 g.
KCl	... 0.5 g.	Glucose	... 30.00 g.
$NaNO_3$	... 2.0 g.	Agar-agar	... 15.00 g.
$MgSO_4$	... 0.5 g.	Distilled water	... 1000 cc.
$pH = 6.8$			

All work was carried out at laboratory temperature which ranged between 26° and 30° C.

For microscopic examination of the organisms, staining was effected with hot carbol-fuchsin.

*Characterization of Bacillus Pandora.*—Characterization tests were carried out on *B. pandora* and its index Number‡ was found to be 5211-U2120-0211.

*Microscopic Features.*—Short rods with slightly rounded ends. Average length  $3.1\mu$  and average diameter  $0.9\mu$ . The largest cell measured had a length of  $4.6\mu$  and a diameter of  $1.2\mu$ . Chains were not common and none containing more than 9 cells were seen.

The organism was motile and the flagella, which were peritrichic, were observed by use of Loeffler's flagella stain. Capsules were proved to be present by staining with Hiss' capsule stain.

The organism was not killed by maintaining cultures at 85° C. for 10 minutes, and endospores were detected by Anjeszky's method, using boiling carbol-fuchsin. The ellipsoid spores had an average length of  $2.3\mu$  and an average diameter of  $1.4\mu$ .

*B. pandora* was gram-positive.

*Cultural Features.*—Growth on agar stroke was moderate at laboratory temperature. The stroke was dull, opaque, without chromogenesis or odor, and no visible changes occurred in the medium. Agar colonies were punctiform, smooth, and white, and growth was slow.

Gelatin colonies were punctiform and white, and growth was slow.

\* This value is arrived at taking the mean value (0.1 per cent.  $P_2O_5$  in latex) of the figures given by Luff (*Chemistry of Rubber*, E. Benn, Ltd., London, 1923, p. 23).

† *Ann. Appl. Biol.*, 13, 595 (1926).

‡ See the descriptive chart of the Society of American Bacteriologists, *J. Bacteriology*, 10, 315 (1925).

**Carbohydrate Reactions.**—Starch was not decomposed after 12 days, and cellulose was unacted upon after 15 days. After inoculation, glucose gave acid without gas, while both acid and gas resulted from lactose and sucrose.

**Biochemical Reactions.**—The organism was found to be a facultative anaerobe. Gelatin was liquefied.

Nitrate was reduced to nitrite without gas evolution. The nitrite was detected by use of sulfanilic acid and  $\alpha$ -naphthylamine in acetic acid. No reaction for nitrite was given by the nitrate used for the tests.

Litmus was completely decolorized within 2 days of inoculation.

Milk was completely coagulated with production of acid. Indole production was observed.

Albumen was digested and ammonia production demonstrated. The hydrogen sulfide test was negative, only a very slight darkening of the lead acetate agar occurring after 12 days.

**Reactions with Hevea Latex Products.**—Solutions were prepared by adding 1 part of latex to 9 parts of boiling water. Tubes were filled with 10 cc. of the solution and heated at 15-lb. pressure for 15 or 30 minutes. After inoculation of the tubes with *B. pandora*, the latex flocculated or coagulated, the surface above the coagulum being alkaline while the serum was acid. The control tubes remained liquid.

After inoculation, latex serum showed acid production without gas evolution.

The latex "carbohydrate" (presumably methyl-*l*-inositol) was prepared by evaporating latex serum to small bulk, taking up with alcohol and evaporating the alcoholic extract to dryness. After inoculation of solutions of this substance, acid was produced but no gas evolution occurred.

**The  $p_H$  Range of *B. Pandora*.**—Van Harpen<sup>23</sup> has obtained the following  $p_H$  values for the points at which the important changes occur during the coagulation of latex.

First liquid zone to first solid zone	4.77 to 5.05
First solid zone to second liquid zone	3.49
Second liquid zone to second solid zone	0.80

In the present investigation, solutions were made containing small quantities of egg albumen and mineral salts, and were made acid and alkaline by the addition of hydrochloric acid and sodium hydroxide, respectively. The  $p_H$  values were determined by the Hellige apparatus.

On the alkaline side, organisms were found in solutions having a  $p_H$  value up to 10.0 but growth was very poor in regions above 9.5. As might be expected from van Harpen's figures, the limit of growth on the acid side is at a  $p_H$  value between 4.0 and 4.5. The  $p_H$  range did not admit of accurate delimitation since growth became very irregular as the end points were approached. However, it can be definitely stated that, while good growth occurs between 4.75 and 9.0, the outside limits of the range are approximately 4.0 and 10.0.

**The Action of *B. Pandora* on Latex.**—While it is generally admitted that latex may be flocculated by the agency of bacteria, some difference of opinion exists as to the process by which the further stage of coagulation is accomplished. De Vries and Beumée-Nieuwland attribute it to the action of a specific enzyme, but Belgrave,<sup>19</sup> Groenewege,<sup>17</sup> and van Harpen<sup>23</sup> are of the opinion that coalescence is brought about by a specific chemical substance which is destroyed by heating. According to van Harpen, however, ammoniated latex does not lose its coalescing action on heating.

Although this subject is hardly within the scope of the present investigation, the results obtained by inoculating latex solutions with *B. pandora* seem to admit of a



more ready explanation on a chemical basis than on considerations of enzyme activity.

In the first place, experiments were carried out on B. or Barrowcliff's Mixture\* which had been subjected to a further sterilization process by heating in an autoclave at 120° C. for 15 or 30 minutes. Such a procedure should ensure the destruction of any enzymes present.

After inoculation of tubes containing B. mixture with the bacillus, flocculation was observed in 2-3 days, but the further change from flocculation to coalescence was a very uncertain process, although in most cases a coherent clot was eventually produced. The serum was generally, but not invariably, milky even after the lapse of two or three weeks.

Stronger solutions of latex (1 part latex to 4 parts water and 1 part latex to 2 parts water) were prepared in a similar manner and, with these mixtures, coagulation occurred more readily and clear sera were obtained.

It was not found possible to sterilize latex by heating it rapidly to 140-150° C. in an autoclave. The latex invariably coagulated when subjected to such treatment.

De Vries has suggested that coagulation in B. mixture after a period of time may be a purely mechanical process; but in the experiments just described it seems possible that coalescence might have been effected by small quantities of some specific chemical substance which escaped complete destruction. It is, however, pressing the question too far to draw conclusions from the present investigation, and always it has to be borne in mind that sterile latex is changed latex.

*Experiments with Sodium Sulfite.*—Solutions were prepared containing small amounts of egg albumen and mineral salts and sodium sulfite† was added in various quantities from a stock solution. In this manner, solutions were prepared whose sulfite content varied between 0.2 and 0.003 per cent.  $\text{Na}_2\text{SO}_3$ . Three days after inoculation with *B. pandora*, the organism was found in large numbers in all the solutions. As some of the solutions tested contained more sulfite than the 0.05 per cent. recommended by Eaton, it is clear that the use of sodium sulfite as an anti-coagulant is not due to any toxic properties which this substance may possess but must be explained along other lines.

That the explanation offered on page 258 is the correct one seems certain from the following experimental results: (a) sulfur dioxide was liberated by the action of dilute lactic acid on sodium sulfite in the cold; (b) latex bacteria were not killed by higher concentrations of sulfur dioxide than that which usually obtains in latex when sodium sulfite is present as an anti-coagulant; (c) sulfur dioxide was evolved from latex containing sulfite.

*Experiments with Ammonia.*—For these experiments, solutions were prepared as in the sulfite experiments, and the ammonia was obtained by dilution of a standard 8.43 N solution.

One series of experiments gave the following results:

Per cent. $\text{NH}_3$ by weight	Growth of <i>B. pandora</i>
3.6	No growth
1.8	Growth very sparse
0.7	Growth fair
0.45	Growth good
More dilute solutions	Growth good

The  $p_H$  values of the solutions containing 3.6 and 1.8 per cent. ammonia were found, by the Hellige apparatus, to be 11.6 and 10.2, respectively.

\* One part of latex added slowly to 9 parts of boiling water and the mixture maintained at boiling temperature for a few minutes.

† The sodium sulfite used in these experiments was analyzed in the Chemical Division of this Institute and found to contain 97.4 per cent.  $\text{Na}_2\text{SO}_3$ .



Latex, then, containing the 0.5 per cent. ammonia recommended by de Vries and Beumée-Nieuwland for good preservation, is not free from bacteria.

There seems to be no doubt that, in ammoniated latex, bacterial action proceeds and the acid produced is neutralized as it is formed. If sufficient ammonia is present initially bacterial activities are to a certain extent neutralized, no acidification of the latex occurs, and hence coagulation does not take place.

*Experiments with Zinc Sulfate.*—The toxicity of zinc salts towards *B. pandora* was tested by inoculation of aqueous solutions containing small amounts of egg albumen and mineral salts and from 0.008 to 1.0 per cent. hydrated zinc sulfate. The results obtained were:

Per cent. of zinc salt  
0.06 and above  
0.03  
0.016 and below

Growth of *B. pandora*  
No growth  
Growth very poor  
Growth very good

### Summary

A bacteriological study has been made of *Hevea* latex and it has been found that one organism predominates. The characters and biochemical reactions of this organism have been studied in detail and, as it does not appear to have been denominated previously, the name *Bacillus pandora* is proposed for it.

*B. pandora* is able to decompose latex substance with production of acid and hence bring about separation of the rubber particles. At a later stage it attacks the proteins with ammonia production and so is responsible for the acid serum and alkaline surface layer observed during the natural coagulation of latex.

The reason for the employment of ammonia and sodium sulfite as latex preservatives is discussed.

### References

- <sup>1</sup> *Biochem. J.*, **3**, 165.
- <sup>2</sup> *Ibid.*, **3**, 351.
- <sup>3</sup> *Proc. Chem. Soc.*, **27**, 54.
- <sup>4</sup> *8th Intern. Congress Appl. Chemistry*, **25**, 597.
- <sup>5</sup> *Agr. Bull. Federated Malay States*, **4**, 26.
- <sup>6</sup> *Meded. Rubberproefstation W. Java*, No. **6**, 1.
- <sup>7</sup> *J. Soc. Chem. Ind.*, **36**, 274.
- <sup>8</sup> *Compt. rend.*, **165**, 123.
- <sup>9</sup> *J. Soc. Chem. Ind.*, **37**, 48T.
- <sup>10</sup> *Agr. Bull. Federated Malay States*, **6**, 374.
- <sup>11</sup> *Ibid.*, **6**, 513.
- <sup>12</sup> *Malayan Agr. J.*, **10**, 151.
- <sup>13</sup> *Ibid.*, **11**, 348.
- <sup>14</sup> *Arch. Rubbercultuur*, **7**, 168.
- <sup>15</sup> *Ibid.*, **8**, 219.
- <sup>16</sup> *Ibid.*, **8**, 233.
- <sup>17</sup> *Ibid.*, **8**, 626.
- <sup>18</sup> De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur*, **8**, 726.
- <sup>19</sup> *Malayan Agr. J.*, **8**, 369.
- <sup>20</sup> De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur*, **9**, 590.
- <sup>21</sup> De Vries and Beumée-Nieuwland, *Ibid.*, **11**, 527.
- <sup>22</sup> De Vries and Beumée-Nieuwland, *Ibid.*, **12**, 454.
- <sup>23</sup> Van Harpen, *Ibid.*, **13**, 44.

### Other Interesting References

- Barritt, *J. Soc. Chem. Ind.*, **33**, 289.  
 Eaton, *Agr. Bull. Federated Malay States*, **5**, 48.  
 Eaton, Frantham, and Day, *Federated Malay States Bull.*, No. **27**, 276.  
 Vernet, *Caoutchouc & gutta-percha*, **17**, 10193.  
 Audubert and Lejeune, *Rev. gén. colloïdes*, **5**, 713.  
 Whitby, "Plantation Rubber and the Testing of Rubber," Chap. 2.

# Notes on Defects in Smoked Sheet and Crepe Rubber

R. G. Fullerton

In the following paragraphs a general account is given of the characteristics and the nature of commonly occurring defects in smoked sheet and crepe rubber, and of the principle underlying methods for their prevention as recommended for estate practice. Many of the defects referred to have no harmful effect on the quality of the rubber after vulcanization, and in the majority of cases the only reasonable excuse for their classification as defects is the unsightly appearance which they impart to the raw product. Since, however, standards of quality at present imposed by the market are based largely on appearance alone, methods have to be devised to prevent the occurrence of these defects.

## A. SMOKED SHEET

### 1. Moulds

Moulds and mildew are higher forms of fungi or microorganisms which, by chemical changes essential to their growth, are capable under favorable conditions of acting on organic substances with which they are in contact. The changes themselves are complicated processes and they are influenced by external conditions such as temperature, moisture, and the presence or absence of oxygen, all of which conditions can be controlled by artificial means. Freshly machined sheet rubber is always rich in the spores of these organisms, and for their growth, adequate supplies of good materials are necessary, even the very small amount of proteinous serum substances which are always present in sheet rubber being sufficiently rich in carbon and nitrogen to foster the growth of mould. A certain amount of nitrogen is also assimilated from the air.

In view of the fact that their growth is influenced by the above-mentioned conditions, methods for the prevention of the development of moulds in the first place aim at storage of the prepared sheet in as dry an atmosphere as possible. The temperature of the atmosphere during storage cannot well be regulated in ordinary practice, nor can the presence of oxygen be avoided since the sheets are always stored in the presence of air, and thus it has become necessary in addition to treat the sheets with antiseptics which retard the development of the moulds. The practice of smoke-drying the freshly machined sheets is extremely beneficial in this respect, since a certain amount of antiseptic creosotic substances contained in the smoke is absorbed by the sheets, and, provided that a sufficiently long period of smoke-curing is employed, there is seldom any necessity for further antiseptic treatment. At present, however, there is an unfortunate tendency to work with shorter periods of smoking than were at one time employed, with the results that the maximum of benefit is not derived from the smoke-curing process, mouldy sheet is thus more in evidence, and additional treatment involving the expenditure of time and money has to be given. It is probable that if the majority of estates were to give the sheet an extra three to four days' smoking much of the present trouble with moulds would be avoided.

The additional treatment referred to consists of the use of *p*-nitrophenol as an antiseptic, there being two different methods whereby the treatment may be carried

out. As the use of this substance is widely practised by estates in Malaya these methods are here described in detail.

(1) *Addition to Latex.*—*p*-Nitrophenol is soluble to the extent of 3 per cent. in water at 40° C. and hence in effecting solution sufficient time must be given for the substance completely to dissolve. A stock solution of 1 per cent. strength is made and the insoluble impurities which are always contained in the commercial product are removed by filtration through a fine cloth. This solution is then added to latex, standardized to a rubber content of 1¼ to 1½ lbs. per gallon, at the rate of 1 volume to 60 volumes of latex. It may be mixed with the latex prior to the addition of the coagulant, or a mixture of the correct quantities of *p*-nitrophenol solution and coagulant may be added. It may be used in conjunction with acetic acid or with formic acid.

(2) *Soaking Method.*—According to this method a 0.1 per cent. stock solution of the antiseptic is made by dissolving it at the rate of 3¼ oz. of the solid to 20 gallons of water, the same precautions being taken to effect a clear solution. The freshly machined sheets are then placed singly in the solution contained in a suitable receptacle and are allowed to soak for half an hour. They are then removed and allowed to drip for about two hours on racks placed in the open in a well-ventilated and shaded site, before being transferred to the smoke-house.

Complete immersion of all the sheets may be ensured by placing boards or planks on top of them, and, by placing them singly in the solution, the whole of the surface of each sheet comes in contact with the antiseptic. Care must be taken, however, not to overcrowd the sheets during immersion merely to economize in space—3¼ oz. of the solid *p*-nitrophenol dissolved in 20 gallons of water is sufficient for the treatment of two batches of sheet of 100 lbs. each. If only one batch of sheet is treated on one day, the solution may be kept for the treatment of a batch of the same size on the following day, the solution being then discarded and a fresh solution used for the treatment of further quantities of sheet.

#### *Notes.—*

(a) *p*-Nitrophenol is usually shipped in drums, and is in the form of a cake containing a certain amount of moisture. The most convenient method of handling it is to place the cake in a suitable receptacle such as a Shanghai Jar for about two days, after which it can easily be crushed to a powder.

(b) Samples of sheet treated with this antiseptic may be sent to the Institute for tests for the development of mould. In doing so, the method of treatment should be described.

(c) The sheet should be packed as soon as possible after removal from the smoke-house, preferably after ten o'clock in the morning when the atmosphere is warm and less damp than in the earlier hours. Sheet which is stored in the open absorbs moisture more rapidly and to a greater extent than sheet which is packed, and moisture absorption increases the liability to mould development. All cases should be sun-dried before being packed and, after packing, should not be stored in direct contact with a cement floor. If sheet has to be stored on the estate and the store is badly sited, it may be necessary to adopt both methods of application of *p*-nitrophenol.

(d) The addition of *p*-nitrophenol directly to the latex before coagulation on certain estates seems to be associated with the production of bubbles in the prepared sheet. The reason for this is not yet definitely known and the subject is at present under investigation by the Institute.

(e) The results of recent experiments on the development of moulds in smoked sheet and in air-dried sheet are to be incorporated in a special bulletin.

## 2. Bubbles

Bubbles in sheet rubber are commonly spoken of as air-bubbles or as air-bells, but in the large majority of cases these bubbles contain larger proportions of other gases such as carbon dioxide, nitrogen, and hydrogen than are normally present in air, and hence it is more correct to speak of them as gas-bubbles. The bubbles usually found in smoked sheet are very small, in some cases microscopic in size, and may be easily observed when the sheet is examined by transmitted light. They may be evenly distributed in the interior of the sheet or may occur in patches, sometimes only on one of the long sides of the sheet, and when examined by reflected light white patches are seen at those parts containing the bubbles, almost giving the impression that the sheet is not completely dry.

In nearly all cases gas-bubbles are formed as the result of fermentative changes which take place either in the latex or in the wet coagulum prior to machining. Rubber latex normally contains a large number of bacteria and other microorganisms which are capable of acting on the serum constituents of the latex so as to produce changes which result in the formation of minute quantities of gases and in the appearance of bubbles in the prepared sheet. These changes may take place in the latex at any stage of the process from tapping of the trees to the stage which immediately precedes the machining of the wet coagulum, and hence it is essential that there is as little delay as possible in the collection of the latex, its transportation from the field to the factory, and thereafter in the addition of the acid coagulant. Fermentative changes are very liable to occur when the trees are tapped after heavy rainfall, as the latex then becomes infected with bacteria which are washed into it from the bark in the vicinity of the tapping cut, and the extent to which fermentation may take place in a latex depends, among many other factors, upon the locality from which it is obtained, the character of the soil in the locality, the season of the year during which tapping is carried out, the system of tapping followed, and the physiological characters of the tree. On some estates the unexpected appearance of bubbles in sheet which for a long time has been free of them, and the equally unexpected disappearance of the trouble, is not an infrequent occurrence.

Methods for the prevention of bubble formation aim at producing in the latex a medium unfavorable to the action of the ferments by the addition of an anti-coagulant substance, in the use of which very satisfactory results have been obtained by the addition of an aqueous solution of sodium sulfite. A stock solution is prepared by dissolving 1 lb. of anhydrous sodium sulfite in 3 gallons of water and is used at the rate of 5 fluid ounces per 4 gallons of latex. This formula applies to its use both in the field and in the factory. Its use serves a double purpose, as not only is it useful in the inhibition of fermentative changes, but it possesses in addition anti-coagulant properties, and thus makes possible the output of a crop consisting of the maximum amount of first grade rubber and the minimum of coagulated "lump." It cannot be too strongly emphasized that fermentation in a latex may begin very soon after tapping, and if these fermentative changes are allowed to proceed to a sufficiently advanced stage while the latex is in the field, the addition of sodium sulfite in the factory only will not prevent the formation of bubbles. In such cases it must be used in the field as described above, and a little of the anti-coagulant solution must also be poured into the cups and a few drops allowed to run down the tapping cut. The addition of a solution of formalin to the latex serves the same purposes as sodium sulfite, and also gives very satisfactory results. In its use, however, precautions have to be taken to ensure that an excess is not added, as otherwise it has a harmful effect on the rubber.

It will be evident from what has been said above that all utensils used for the

handling of the latex both in the field and in the factory must be clean, and that a plentiful supply of clean water for factory operations is essential. In this connection it may be pointed out that it is a matter of great difficulty to remove small pieces of coagulated rubber and fermentable serum products which lodge in the fissures of wooden coagulating tanks and partition boards, and this is the basis of one of the arguments which can be advanced in opposition to the use of such tanks. The same remarks apply with equal force to the case of tanks lined with glazed tiles unless the interstices between the tiles are filled in with a suitable cement. Particulars of such cements may be had on application to the Institute. When coagulation is carried out in large tanks it is often found that bubbles occur on only one of the long sides of the sheet. This corresponds to the side of the coagulum which was nearest to the bottom of the tank, and the bubbles are produced as the result of anaerobic fermentation—that is, fermentation which takes place in the absence of air.

In preventing bubble formation care must be taken to use the correct quantity of acid coagulant and to ensure that thorough mixing of the coagulant and latex is effected.

Reference may be made to what are commonly spoken of as "blisters," which are produced as the result of overheating in the smoke-house particularly in the early stages of the smoke-curing process.

### 3. "Rust"

It is sometimes found that on stretching a piece of smoked sheet rubber and allowing it to recover after stretching, a brownish colored powder appears on the surface at the part which has been subjected to stretching, while in a few cases the powder may be observed on the surface even before the sheet is stretched. On account of its appearance this powder is commonly spoken of as "rust," and is probably formed as the result of the decomposition by microorganisms of the serum substances which exude from the sheet after it has been machined. An investigation is at present being carried out by the Institute with a view to the isolation and the identification of the microorganisms responsible for this decomposition and with the object of establishing the chemical nature of the constituents of the "rust."

It has already been shown that of a batch of sheets prepared on the same day and under the same conditions, those which were stored in a moist atmosphere for a period of two days after machining became covered with a thick coating of "rust," while those of the same batch stored in a moist atmosphere containing a little of the vapor of formalin were entirely free from this defect. This result and others already obtained indicate that the presence of moisture is favorable to the growth of "rust," and that its development may be checked by suitable antiseptic treatment of the freshly machined sheets. The temperature of the atmosphere usually maintained inside a smoke-house is also very favorable to its growth.

In the majority of cases, therefore, methods for the prevention of "rust" aim at rapid surface-drying of the sheet, and hence it is recommended that, after machining, they be hung to drip for about two hours on racks placed in the open air and in a shaded site, after which they should be transferred to the smoke-house, the temperature of which in the initial stages of smoke-curing should be higher than in the final stages. The temperature should be maintained between 110° and 120° F. In more severe cases an antiseptic must be used, and in this connection it has been found that soaking the freshly machined sheets for half an hour in an 0.1 per cent. aqueous solution of *p*-nitrophenol, the treatment being the same as that used for the prevention of moulds, is effective in preventing the



formation of "rust." After removal from the bath of *p*-nitrophenol solution, the sheets are allowed to drip in the open for two hours, as outlined above, before being transferred to the smoke-house.

## B. CREPE

### 1. "Spot" Disease

Pigmented spots in crepe rubber are produced by the growth under suitable conditions of fungi, the spores of which are always present in abundance in freshly machined crepe rubber. These spots may be of different colors—red, orange, yellow, blue, green, violet, and black—although violet spots are of the most frequent occurrence. As in the case of moulds on sheet rubber these fungi require suitable conditions of temperature and moisture for their development, although in the latter case simpler methods suffice to prevent their growth.

Bearing in mind that only in the presence of air and under favorable conditions of temperature and moisture will the fungi develop, it will be seen that the following factors will promote the production of colored spots on crepe.

(a) *Delay in Transferring the Freshly-Machined Crepe to the Drying Sheds.*—It is necessary that there be as little delay as possible in this operation, and the crepe should be hung in the drying sheds on the day on which it is machined. The object should be to dry the crepe as quickly as possible in order to produce conditions inimicable to the growth of the organisms at an early stage. Very many cases of "spot" disease have been found to be due to neglect in this direction.

(b) *Inefficient Ventilation in the Drying Sheds.*—Drying sheds are best constructed of corrugated iron which is a good conductor of heat, and the ventilation should be such as to ensure a good upward current of air within the drying chambers.

(c) *Excess of Sodium Bisulfite.*—In crepe manufacture sodium bisulfite is widely used in order to produce a crepe of pale color. It is a hygroscopic salt, and if too large a quantity is added to the latex, it will absorb moisture from the atmosphere and retain it on the surface of the crepe.

(d) *Insufficiency of Sodium Bisulfite.*—Sodium bisulfite has an antiseptic action toward fungi and the correct quantity must be added to the latex before coagulation. The sodium bisulfite should be added at the rate of 1 lb. of the salt dissolved in 10 gallons of cold water to 100 gallons of latex standardized to a rubber content of 1½ lbs. per gallon in the case of pale crepe manufacture, and 2½ lbs. per gallon in the case of sole crepe manufacture.

(e) *Excessive Thickness of the Crepe.*—A thick crepe contains a higher proportion of moisture than thin crepe, and hence the coagulum should be machined as thinly as is consistent with the production of a crepe of good even texture.

(f) *Storage of the Dry Crepe under Damp Conditions.*—Storage in direct contact with a cement floor is frequently a cause of dampness of the finished crepe.

If the recommendations outlined above are followed there is seldom any necessity for further treatment. In special cases, however, an antiseptic substance must be used, an effective method being to soak the freshly machined crepe for half an hour in a bath of formalin of 1 per cent. strength before transferring it to the drying sheds. This treatment is not a sufficient safeguard in itself, and attention must be paid to the other details of manufacture to which reference is made above.

### 2. Tackiness

Tackiness or stickiness in first grade rubber is very seldom met with at the present day, whereas a slight stickiness of the surface of lower grade crepes such



as "compo" crepe and rather more severe cases of tackiness in "earth scrap" crepes are of frequent occurrence. Rubber which has become tacky is rightly regarded as defective, since tackiness involves changes in the chemical and physical structure of the rubber, which in severe cases are sufficient to affect detrimentally the quality of the rubber after vulcanization. Such deterioration may be brought about in various ways but it is sufficient here to consider only those which occur in ordinary plantation practice.

In the case of the "earth scrap" and "bark shavings" from which lower grade crepes are manufactured, the rubber before arrival at the factory becomes infected with a large number of microorganisms which are found in the soil and in the bark of the tree, and which are capable of producing fermentative changes in the rubber resulting in a condition of tackiness of the whole or part, depending on the extent to which these changes have taken place. Moreover, it is known that in the presence of air, exposure to the sun's rays and to heat produces this kind of deterioration, and it is evident that the raw material for the preparation of lower grades is so exposed while it is in the field. Hence, since rubber which is subjected to excessive mastication between the machine rolls is liable to become tacky, it will be appreciated that in dealing with lower grades the extent of the mastication treatment is a very important point indeed, the raw material on arrival at the factory having in the majority of cases already deteriorated to a considerable extent. Lower grade crepes should therefore be thicker than crepes of the first grade in order that the rubber may receive as little machining as is consistent with the production of a crepe of good appearance and uniform texture. In addition to the usual battery of crepeing machines, a scrap-washer is essential for the manufacture of these grades, and it is well to collect the raw material from the fields as frequently as possible, to cleanse it thoroughly on arrival at the factory, and, if machining cannot be proceeded with until some time afterward, to store it under water, which must be changed periodically in order to keep it fresh and to remove dissolved putrescible substances. It is often found that if large piles of "bark shavings" are left standing exposed to the air for a few days the interior of the mass becomes quite hot, and this generation of heat may be sufficient to lead to tackiness in the final product. When practicable, the raw material should be converted to crepe form as soon as possible.

Tackiness may also be brought about by specific chemical agents, the presence of minute quantities of copper in the rubber being sufficient to bring about this deterioration. Contamination with copper is frequently brought about by brass filings carried by oil from worn bearings which accidentally comes in contact with the rubber while it is being machined. Again, acetic acid such as is used for coagulation occasionally contains traces of copper salts, since in the preparation of the acid of commerce it is usual to distil it from copper stills. Even as small a quantity as 0.01 per cent. of a copper salt added to latex is sufficient to produce deterioration in the final product.

### 3. Yellow Crepe

It is frequently found that the latex from young trees is of a noticeably yellow color, while a yellow crepe is often produced from latex obtained during the early stages of tapping on a new cut. Again, in the periodic system of tapping the crepe may be yellow in color for some days, when tapping is commenced after a period of rest. The yellow color is due to the presence of a naturally occurring vegetable pigment in the latex, and it may be said here that investigations have been carried out by the Institute with the object of identifying this pigment and that the results will be published shortly in bulletin form.

An increase in the amount of sodium bisulfite added to the latex will not reduce the depth of the color, but by the usual methods of fractional coagulation adopted in the manufacture of sole crepe, most of the yellowing coloring matter may be removed in the first coagulum, a very pale colored crepe being obtained from the second fraction.

# The Pneumatic Tire in Heavy Transport<sup>1</sup>

A. Healey and W. Bond

## Introduction

The last seven years have seen the beginning of a new era in heavy transport. Hitherto road transport had been confined to services where it was not economical to lay down a railway track, where the distances were comparatively short and loads comparatively light, and where the lorry could handle goods in special ways not possible on the railway, *e. g.*, in the removal of merchandise direct from gate to gate of factories without wasting time.

Today the situation is quite different. The reduced profits of railway companies are ascribed to the competition of road transport and those companies are extending their sphere of operation, not so much by building new tracks, but by the simpler and less costly expedient of running road vehicles.

There can be no doubt that the tire manufacturers have been largely responsible for this revolution. Their production of the giant pneumatic tire was the first step, for without this accessory, modern road transport, and modern types of road vehicles, would be unthinkable. The technical reasons for this provide interesting study to engineers, and should indeed be properly understood by all who are interested in the engineering and operating sides of transport problems, if the fullest advantage of tire equipment is to be obtained.

## History

The first pneumatics to be used for commercial vehicles were called, in Great Britain, "Giant" tires. The word "Giant" is now commonly used to describe a tire adapted to the needs of commercial vehicles as distinct from private motor cars, and having a nominal cross-section of 6 in. or more.

The date of the first appearance of giant tires is somewhat obscure. There is some evidence that experiments were being conducted in the United States of America about the year 1908, and that at this time some tires having the nominal size 38 by 6 were produced.

Between 1908 and 1916 experiments were being made with tires of different sections, 7 in., 8 in., 9 in., 10 in., and 12 in., but these made little progress owing to the fundamental difficulties of the "canvas" construction, "cord" tires not then being established even for motor-car tires.

The giant tire really awaited the coming of cord construction, and in 1916 the adoption of cord fabric made it evident that the problem of providing giant pneumatic tires could be regarded as solved in the basic sense, though there were considerable practical difficulties in making them on account of their thickness.

The first practical application of such tires appears to be their adoption in 1917 upon an experimental motor truck service on a 1400-mile round trip between Boston and Akron, U. S. A., and in the next year or two a certain uniformity in

<sup>1</sup> A paper read before the Institution of Automobile Engineers at Leeds on December 4, 1929. Published by the permission of the Institution of Automobile Engineers, Watgate House, Adelphi, London, W. C. 2.

size practice came about, the sizes fixed upon and coming into use by the end of 1919 in the United States being 36 by 6, 38 by 7, 40 by 8, 42 by 9, and 44 by 10.

It is clear that though such tires could be procured in the United States, there was a good deal of hesitation about their acceptance, chiefly on account of cost and the alleged unreliability, and in a paper contributed by S. V. Norton of the B. F. Goodrich Company, in June, 1920, entitled "Motor Truck Efficiency as Related to Solid and Pneumatic Tires," the author, in a critical examination of the relation between solids and pneumatics, notes that the accepted field for pneumatics was on trucks up to 1½ tons capacity, but that for anything greater the solid tires are to be preferred. He also states regarding giant tires that "while I realize that no mechanical device is as resilient as air, we have a long way to go before we overcome the difficulties of making it serve us acceptably in puncture-proof and fool-proof rubber tires, although the industry is making notable progress in this direction."

There was agreement in 1920 that pneumatic truck tires had been perfected only in sizes up to 8 in., and that larger tires than this were then regarded as in the experimental stages.

Attention was also commencing to be drawn to the desirability of designing trucks especially for pneumatics, but the number of such trucks in existence in 1920 was very limited indeed.

In England, owing to the war years, development of giant pneumatic tires was unable to proceed, and the first giant tires to appear as commercially proved articles were brought out by the Dunlop Company. The first were shown in a price list dated October, 1921, namely, 36 by 6 and 40 by 8.

In Great Britain and the United States the "clinch" "beaded-edge" type of giant tires have never been adopted in any important degree as original equipment, though there was in Great Britain some occasional use on vehicles converted from solid tires.

On the continent of Europe the beaded-edge tires had a much greater measure of acceptance, but today the "straight-side" or wired type of tire has proved so much more suitable for the conditions imposed by heavy transport that the "beaded-edge" tire has gone out of use, and the original equipment of vehicles is for all practical purposes confined to tires of the wired type. The only demand for beaded-edge tires is now for replacement purposes on older vehicles.

It would be a very laborious and difficult task to trace the gradual increase in the adoption of giant pneumatic tires year by year, and probably not useful for the purpose of this paper. It may, however, be said that in the main the pioneers in the use of such tires were not the vehicle makers, but rather vehicle users who were prepared to experiment in changing over from solids to pneumatics, especially in the passenger-carrying industry.

It was soon found that if in any local area a pneumatic-tired bus or char-a-banc was available, no business could be got for a solid-tired vehicle, and this led not only to many thousands of conversions, but to imperative demands for new vehicles originally equipped and designed for pneumatic tires.

At the date of this paper the position in Great Britain is of the following order in regard to the equipment of new vehicles:

Passenger-carrying heavy vehicles from 3 cwt. rating and upward to the heaviest double-deck buses are 100 per cent. pneumatics.

For goods-carrying vehicles, up to 3 tons rating, 100 per cent. pneumatics.

For goods-carrying vehicles, over 3 tons, about 50 per cent. pneumatics, but the proportion is rapidly advancing. It is anticipated that within two years at most all goods-carrying vehicles up to 7 tons rating will be pneumatic tired.

Above 7 tons the position is problematical. Pneumatic tires will probably become the sole equipment for front wheels, but it is in this class (including the heavy steam vehicle) that the use of the solid tire will survive longest, chiefly because the limited speed at which these vehicles are legally entitled to travel does not permit one of the main advantages of pneumatic tires to be utilized.

### A Comparison of Solid and Pneumatic Tires

The giant pneumatic tire, like its smaller predecessors for automobiles, was not introduced to supply a demand, but rather created a demand by virtue of its special characteristics. As already mentioned, these characteristics were the *sine qua non* of the development of modern road transport, which is both "heavy" and "fast." This development was not due to any obvious and simple fact, such as reduced cost, for pneumatic tires have always been, and still are, much more expensive than the solid rubber tires they replace. Even the tire cost per mile

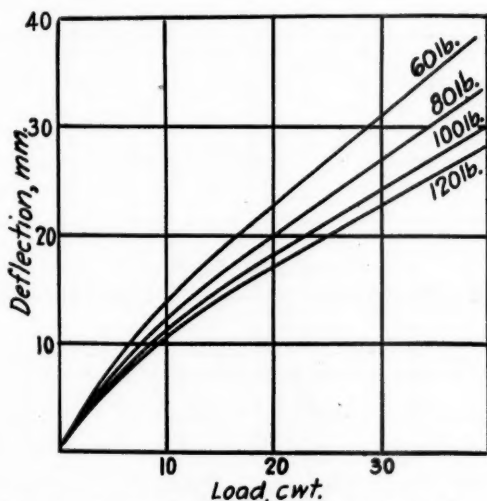


Figure 1—Load-Deflection Curves of 8 in. Giant Pneumatic Tire at Different Pressures

run under equal conditions is higher for "pneumatics" than for "solids." Pneumatics, at any rate during the earlier stages of development, were not less, but more liable to cause involuntary stops, and, in addition, were prohibited by some public bodies because of the possibly serious effects of a burst tire. For what reason, then, did the pneumatic tire attain its supremacy over the solid? The answer is twofold: (1) the pneumatic is capable of running at more than twice the speed of the solid tire; (2) the pneumatic gives a much greater "cushioning" from road shocks.

It is difficult to say which of the two factors is the more important; both are fundamental. The solid tire was known to have been taxed to its limit in the matter of speed, and "blow-outs" due to generation of frictional heat within the body of the tire were a common cause of failure. Every effort of the tire manufacturers to reduce the internal friction has been made, but this trouble still limits the speed of vehicles. (Specially designed tires for "high speed" were even offered to the public, but still speed was limited. Vehicles were designed and loads and

speeds arranged so as to fall just within the safety zone of the solid tire—and any overspeeding or overloading usually proved too much for it.)

At the same time, efforts were made to get greater cushioning by altering the sectional shape of the solid tire, and by making it of a softer rubber compound. The best that can be done in these directions has probably been reached already, and the pneumatic tire excels the “cushion” solid, and the high-speed solid tire, each in its special domain. It far out-cushions the cushion solid, and far out-speeds the high-speed solid.

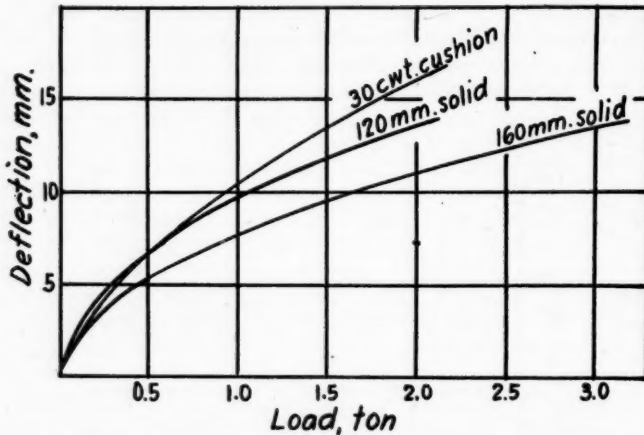


Figure 2—Load-Deflection Curves of Solid and Cushion Tires

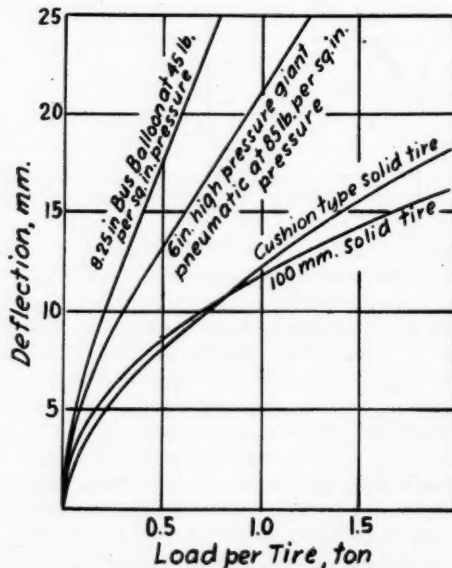


Figure 3—Alternative Tire Equipment for an Axle Load of 2 Tons

Comparative load-deflection curves.



From the standpoint of the engineer, the precise facts and the technical explanations are of great interest, and are therefore discussed in some detail.

**Cushioning Effect of Tires.**—Contrary to popular belief, the cushioning effect of a tire is not measured by its ability to absorb obstacles, but by its deflectability under load, on a plane surface. This problem has been discussed at length in a previous paper by one of the authors,\* and will not now be enlarged upon. It is sufficient to say in passing that an isolated obstacle which can be absorbed by a tire causes no appreciable shock to a vehicle. Serious shocks are produced by irregularities of the road surface, such as pot-holes, which cause the axle of the vehicle to be "jerked" upward.

The "deflection" or "compression" of a tire under load can be measured easily and accurately, and in Figs. 1, 2, and 3 some typical curves are given, showing the load-deflection relation. It will be noticed that for the pneumatic tire the relation between load and deflection is simply proportional (for practical loads)—i. e., the pneumatic tire has a constant spring characteristic, and may be represented mechanically as a spiral spring. On the other hand, the solid tire (Fig. 2) gradually "stiffens" under increasing load, and never reaches a constant characteristic. This is a very serious drawback to the solid tire, for in reality, at the moments when it is called upon to function to the fullest extent—i. e., when already compressed under load, and meeting a road hump—it behaves almost as a rigid structure.

The extent to which the normal "cushion" tire improves upon the solid, and to which the pneumatic improves upon both, is represented in Fig. 3, and for convenience the spring strengths are tabulated below:

	Measure of Cushioning Effect (% Inverse of Spring Strength)	
Solid.....	2	(The units are deflection in tenth millimeters per cwt. increase in load when the normal load is already applied to the tire.)
Cushion.....	4	
Pneumatic.....	8	
Bus Balloon.....	10	

(The last named is discussed in a separate section.)

In order to bring home to the engineer what these figures mean, the corresponding spiral steel springs have been drawn to scale in Fig. 3a.

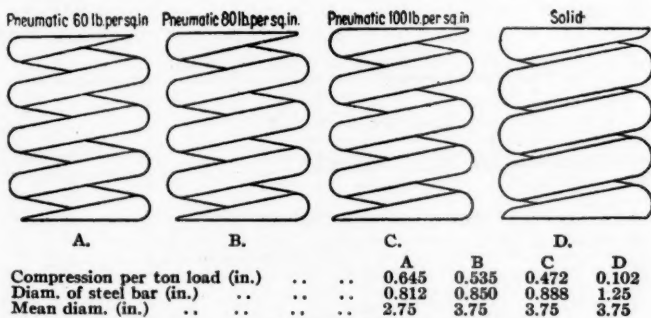


Figure 3a

Remembering that little is to be expected in the way of improvements to cushion or to solid tires, the figures have added significance, and the advantage of the giant pneumatic in cushioning capacity is obvious.

**Why Pneumatics Can Be Run at High Speeds.**—There seems to be a considerable

\* See *Proc. I. A. E.*, XIX, p. 26.

amount of misunderstanding generally with regard to this point. It is often assumed that the pneumatic tire generates less heat within itself than does the solid, because it is an "air" tire, and "air" has very little viscosity (internal friction). When precise measurements are made, however, it is found that, under comparable conditions, the pneumatic consumes more power, during running, than does the solid, as indicated in Table I.

TABLE I

	Approximate Horse Power Consumed by Tire	
	At 18 m. p. h.	At 33 m. p. h.
Solid.....	0.60	1.12
Pneumatic.....	0.66	1.30

This power must reappear as heat, and consequently more heat must be generated in the pneumatic than in the solid tire. Glancing at Fig. 4 illustrating to

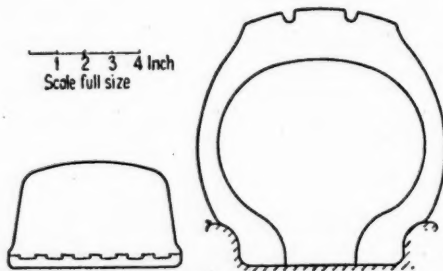


Figure 4—Comparison of Giant Pneumatic and Solid Tires to Carry the Same Load

scale the corresponding cross-sections of tires of each type, it will be observed that there is far more opportunity for heat to escape from the pneumatic than from the solid tire. The point of maximum generation of heat is 41 mm. from the surface in the case of the solid and 27 mm. in the case of the pneumatic. Rubber is a notoriously bad conductor of heat, and even the best conducting rubber compounds that can be found have very low conductivities.

#### THERMAL CONDUCTIVITIES

Best conducting rubber compound for solid tires.....	0.00087
Pure rubber.....	0.00030
Wood (dry).....	0.0005
Cotton wool (example of poor conductor).....	0.00004
Copper (example of good conductor).....	0.9
Steel.....	0.1

In this highly technical consideration, the secret of the pneumatic-tire success is to be found. Solid tires have been made with the highest possible conductivity (0.00087) consistent with satisfactory wear, and other essential features.

At the same time, rubber compounds with extremely low internal friction have been used so low that on distortion only 7 per cent. of energy is consumed. Even in these ideal circumstances, a quite ordinary giant pneumatic tire has much greater speed capabilities, as well as greater cushioning effect.

The rise in temperature in the two types of tires has been studied in great detail by some tire manufacturers, and some representative curves are shown in Fig. 5.

Two solid tires (A and B), one (A) having an ideal rubber compound from the heat generation point of view, and the other (B) having better wearing qualities but greater heat generation, were run under similar conditions on a circular drum. It will be seen that very high temperatures are reached in each case, and that in

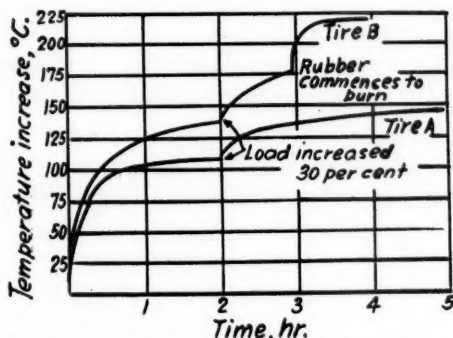
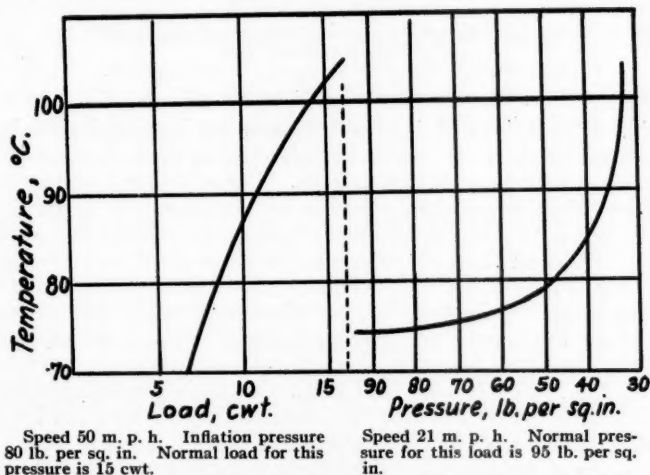


Figure 5—Rise of Temperature in Two Solid Tires Run at 22 M. P. H.

the case of (B) the temperature was so high ( $175^{\circ}\text{C}.$ ) that the rubber was disintegrated and the tire destroyed; yet the speed was only 22 miles per hour. Corresponding curves for giant pneumatic have not been obtained, because of experimental difficulties, but it is found that after an hour's run, a giant pneumatic tire reaches a certain maximum temperature, and further running produces no increase. Turning to Fig. 6, the curve on the right shows that under proper conditions of load and pressure, a particular pneumatic tire reaches a maximum temperature of about  $75^{\circ}\text{C}.$ , and even when inflated to one-half the correct pressure only, the temperature reached is only  $80^{\circ}\text{C}.$  The speed was practically the same



Speed 50 m. p. h. Inflation pressure 80 lb. per sq. in. Normal load for this pressure is 15 cwt.

Speed 21 m. p. h. Normal pressure for this load is 95 lb. per sq. in.

Figure 6—Effect of Load and Inflation Pressure on Temperature Attained by Giant Pneumatic Tire

as for the solid tire. Fig. 6 (left) indicates the very serious effect of overloading, the temperature rising by  $10^{\circ}\text{C}$ . for an increase of 3 cwt. in the load carried. Fig. 7 shows the effect of increasing speed on the giant pneumatic, at 35 miles per hour the maximum temperature being  $107^{\circ}\text{C}$ .

These curves and figures are merely illustrative. Tire manufacturers, and, indeed, vehicle owners, also, know that on solid tires it is impracticable to maintain an average speed under load for a long run, of more than 16 to 18 miles per hour, while on pneumatics the average may easily be higher than 30 miles per hour, the figure being determined by other factors, not by the tires.

It is pertinent to ask, if the pneumatic tire offers such remarkable advantages, why did solid tires ever attain such wide usage? Why were not pneumatics thought of before?

In the section under the heading "History," allusion is made to the "cord" construction, which is essential to the giant pneumatic. Canvas in a tire generates a large amount of heat, and this heat caused early failure even of tires no larger

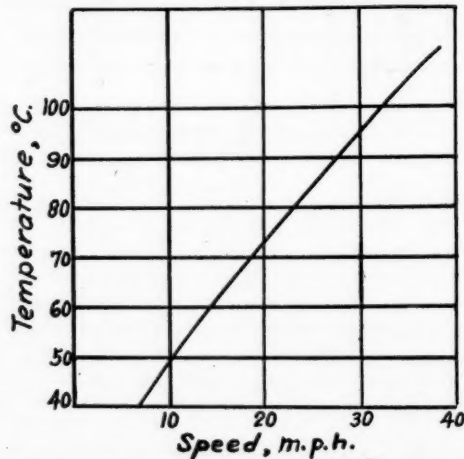


Figure 7—Effect of Speed on Temperature Attained by Giant Pneumatic Tire  
Load 18 cwt.; Pressure 60 lb. per sq. in. ( $16\frac{1}{2}$  per cent. overload).

than  $4\frac{1}{2}$  in. "Cord" is much less liable to generate heat, and gives longer life for other reasons as well. It may be imagined what would happen in an 8-in. giant pneumatic, with 14 or 16 canvas plies. The structure would be burned in a short time at 30 miles per hour. Yet the remarkable results obtained from the "cord" could not be used to full advantage without a revolution in manufacturing methods even for small tires, necessitating much new plant, and years of experiment and research. This having been accomplished for small tires, the way was open for giants of cord construction, but there were still further difficulties of manufacture due to the great thickness of the tires and the tendency to irregular vulcanization.

*Relative Cost of Pneumatic and Solid Tires.*—In Table IIa are reproduced some figures which have been previously published, and which have not been arrived at by tire manufacturers, but by vehicle operators.

The figures are of considerable interest. In spite of the statement above that the power consumed by solids is less than that consumed by pneumatics, the

gasoline consumption is shown to be less for pneumatics. This is accounted for by two principal facts:

- (a) On pneumatics a more economical engine speed is maintained.
- (b) On pneumatics there is less waste of power in spring deflection, and general vibrations of the vehicle.

The totals show an advantage of cost with the solid tire, but some very important items of cost have not been included. For example, in order to carry 100 tons of materials for a distance of 100 miles in one day, more vehicles will be required if solid tires are used. A 5-ton vehicle on pneumatics could run 200 miles in a day with no more effort than a similar vehicle on solids running 120 miles. Therefore, in the case in question, 10 pneumatic-tired vehicles or 16.7 solid-tired vehicles

TABLE IIa

OPERATING COSTS OF COMMERCIAL VEHICLES ON PNEUMATICS AND ON SOLIDS  
Extracted from standard tables published by the *Commercial Motor*, January, 1929

	1 1/4 Tons		2 Tons		3 Tons		4 Tons		5 Tons	
	Pn.	S.	Pn.	S.	Pn.	S.	Pn.	S.	Pn.	S.
Fuel.....	1.16	1.22	1.26	1.33	1.54	1.68	1.75	1.85	2.00	2.10
Lubricants.....	0.10	0.11	0.12	0.13	0.17	0.18	0.20	0.21	0.24	0.26
Tires.....	0.80	0.45	1.13	0.50	1.60	0.65	1.80	0.80	2.07	0.90
Maintenance.....	0.80	1.10	0.88	1.23	1.10	1.42	1.20	1.57	1.30	1.70
Depreciation.....	0.53	0.58	0.80	0.93	1.12	1.20	1.28	1.40	1.52	1.65
Total.....	3.39	3.46	4.19	4.12	5.53	5.13	6.23	5.83	7.13	6.61

Prices based on pence per mile.

It must be clearly understood that the figures embodied in this table are the average results of the working of vehicles of all makes, operating in different trades, over all classes of roads and under different conditions. In specific instances, where circumstances of operation are better or worse than the average, allowance can be made.

would be required. There is thus a less charge for interest on investment for the former type. Again, a driver's wages of, say, £3 is distributed over 1000 miles in the case of pneumatic tires, and over only 600 miles in the case of solids. This means an advantage of practically 0.5d. per mile for pneumatics. Adding this to garage space, overheads, insurance, and other items which will be obvious to the user, it is clear that there is a substantial saving in all-in cost, by using pneumatic tires.

### The Giant Pneumatic Critically Examined

Is the well-known range, 32 by 6, 34 by 7, 36 by 8, etc., the most efficient, or is there a more suitable one? Are the tires mentioned too large, too small, too highly inflated, or underinflated?

These questions can best be answered by comparing the range with what is known as the Bus Balloon range—38 by 8.25, 38 by 9.00, 40 by 10.50, etc.

The Bus Balloon is the name given to the type of tire which bears the same relation to the ordinary giant pneumatic tire as the balloon motor car tire does to the old high-pressure tire. It is designed to run at a lower inflation pressure than the normal tire, and is of substantially greater size.

The theory of the bus balloon tire will be considered in relation to the general theory of the pneumatic tire.

*General Theory of the Pneumatic Tire.*—The pneumatic tire is able to function by virtue of the bending of its walls under load. This bending takes place in each part of the tire once per revolution, even on smooth roads. The capacity of the walls of the tire to withstand bending without being disintegrated determines its

load-carrying capacity, and the appropriate load to be carried for any inflation pressure.

It is found after long experience that the high-pressure, straight-side type of tire (i. e. such nominal sizes as 30 by 3, 30 by 3 $\frac{1}{2}$ , 31 by 4, 32 by 4 $\frac{1}{2}$ , 33 by 5) is capable of functioning with a vertical deflection of 15 per cent. of the actual tire height. That is to say, for example, that a tire of 4 in. actual height may safely run under a load which causes a 0.6 in. depression of the tread toward the rim. The percentage of 15, however, does not apply to other types of tires, and the situation is set out in Table II:

TABLE II

	Allowable Deflection Per Cent.	Ratio of Tire Thickness to Sectional Width
High pressure str. side.....	15	15.0
Balloon—such as 31 $\times$ 5.25.....	20	21.5
Giant.....	13	12.7
Bus balloon.....	17	15.9

The second column of figures represents the approximate proportions of the various types of tires, the giants having thick walls, and the car balloons thin

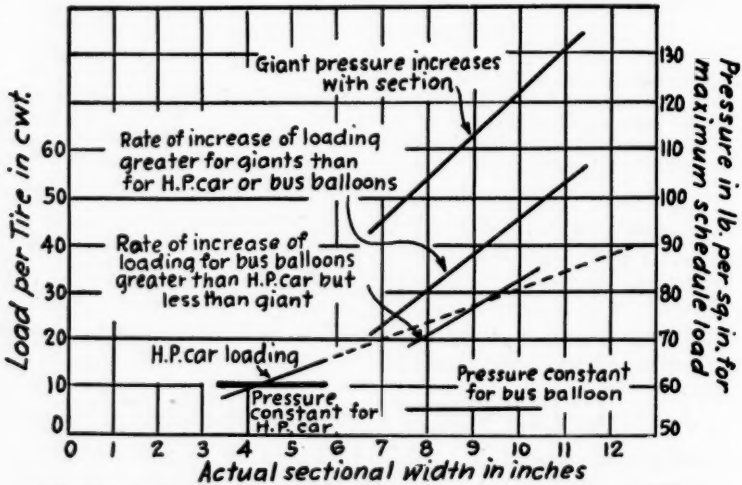


Figure 8—Load-Section and Pressure-Section Comparisons on Pneumatic Covers

walls, relative to their general dimensions. These figures are rough approximations, but they serve to indicate a difference between the giant type and the high-pressure motor-car sizes of which it is alleged to be a continuation.

The close relation between the two columns is not surprising; it is just what would be expected from any other type of structure.

Turning now to the relation between size of tire and maximum load, we again find a discontinuity in passing from the 5 in. nominal to the 6 in. nominal size. The giant sizes carry a proportionately heavier load than the smaller sizes, and naturally have to run at a higher inflation pressure. These facts are illustrated in Fig. 8, from which it will also be observed that the bus balloon tires more nearly fall in line with the car high-pressure range.



It is not difficult to understand why the giant range was not a logical continuation of the smaller range from 3 in. to 5 in. The reasons can be summarized briefly:

(a) The smaller sizes made the motor car possible, and grew up side by side with it free from competition.

(b) The giant range had to enter a market established on solid tires—and consequently cost, mileage, freedom from puncture and damage, clearances, etc., had to be thought of. The most ideal combination, of tire and vehicle, the *designed* combination had to wait for a few years.

It is only recently that the tire manufacturers have begun to feel their way toward the ideal, and the bus balloon tire is a result. This type, though more consistent with the high-pressure motor-car type, has not yet established itself. Unless a considerable amount of extra care is taken of the tires, they are very susceptible to rapid tread wear and damage. A slight underinflation, or a slight misalignment of a wheel produces a serious loss of tire mileage.

It may ultimately be found that both these ranges of tires need not be maintained in existence.

Some compromise between them may be desirable. In Germany, for example, there are already signs of this in a proposal to drop the high-pressure range altogether, and increase to some extent the loads and pressures for the balloon tires, still leaving the pressures considerably lower than those hitherto used in the high-pressure range.

This is, however, a matter for the future, and is merely mentioned to indicate the fact that there is nothing final about the present situation in respect to sizes, loading, and inflation pressure.

### The Performance of Giant Pneumatic Tires

One of the difficulties of the tire manufacturer is to explain why the performance of his tires varies so much. Such explanations were for a long time regarded as excuses for bad workmanship, but the facts are now being generally accepted.

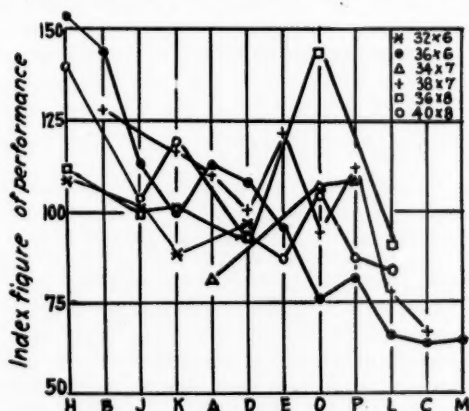


Figure 9—Comparison of Fleets (1928)

The mileage to be got out of a pneumatic tire depends primarily on the skill and care exercised in its design and manufacture. But there are other factors, independent of the tire, which can multiply or divide mileage by 10, and add or subtract miles by the tens of thousands.

This will become clear from what follows. An analysis of the performance of tires on twelve fleets of vehicles during 1928 has been made, and the results tabulated and shown graphically in Fig. 9, and the conditions under which the fleets operated are shown in Table III, in which the block capitals are codes for the different fleets. There is some irregularity among the results, but the considerable variation in average mileage from fleet to fleet is unmistakable.

TABLE III

Fleet	Roads	Maintenance
H	Good. Flat	Fair
B	Good	Excellent
J	Variable—mainly good	Good
K	Bad. Hilly in parts	Very good
A	Narrow winding; not hilly	Excellent
D	Good. Undulating	Not good
E	Gradients in most parts	Good
O	Fairly hilly	Good
P	Winding; few hills	Good
L	Hilly	Fair
M	Very hilly	Bad
C	Very winding and hilly	Not good

An analysis of the causes of removal is interesting. In Table IV for the 36 by 6 tires—the biggest group—it will be noticed that removals in the best and worst fleets are mainly due to tread wear, but the worst fleets show structural failures and accidental damage. The two best fleets show no structural failures and very little accidental damage.

TABLE IV

Fleet	Worn Out	Structural Failure	Cuts and Punctures	Accidental Damage
H	87.5	..	12.5	..
B	87.8	..	2.4	4.9
J	51.8	3.8	26.9	10.5
K	77.1	..	10.4	10.4
A	54.0	8.1	21.6	16.2
D	33.1	15.4	23.8	14.6
E	86.3	7.8	5.9	..
O	86.9	1.5	7.6	3.1
P	63.8	3.6	13.3	14.8
L	84.5	7.7	..	..
M	81.5	3.7	..	11.1
C	89.6	0.95	..	9.5

### Legislation

As already stated, the main advantages of giant pneumatic tires arise out of the increased cushioning and speed permitted by the pneumatic principle as compared with all other forms of tire equipment, whether composed of elastic materials or otherwise. In exactly the same way, the solid rubber tire, by reason of its greater cushioning, has advantages over tires not made of elastic material.

There is no need to enlarge upon the advantages, to the vehicle and to those in charge of its operation, of maximum cushioning. Any improvement in the cushioning of the vehicle, *i. e.*, which relieves the vehicle from shock, also has an exactly similar relieving effect upon the road surface, and this has a most important bearing upon the cost of road development and maintenance. It is obviously to the interest of all road authorities to encourage every form of motor transport to adopt tires which cause the least destruction to roads, and this is now being done to a

much larger extent than is generally appreciated. The general line of encouragement takes the form of legislation or regulation giving some advantages to the owners of pneumatic-tired vehicles as compared with owners of vehicles on solid tires, and also advantages to the latter as compared with those on iron or non-elastic tires.

The regulations usually take the form of prohibition of transport on any other than pneumatic tires, discouragement of non-pneumatics by extra tax or lower speed, strict regulations as to size of tire and weight to be carried when non-pneumatic tires are used, and miscellaneous means of obtaining the same result.

Powers are often possessed by local authorities in any one country which mean that the regulations in that country are not necessarily uniform in all districts, and it is a matter of some difficulty to get accurate information in regard to the world situation.

Records of regulations or legislation exist in connection with at least 72 different countries or territories, and a general summary showing the manner in which these regulations act is as follows:

	Private Cars	Trucks
Metal tires prohibited.....	2	5
Rubber tires compulsory.....	7	2
Pneumatic tires compulsory.....	4	4
Extra tax on solid tires.....	9	35
Extra speed for pneumatics.....	3	7
Miscellaneous regulations, defining size, weight, etc.....	15	26

The general tendency of regulations governing tire equipment is to increase in scope and in repressive effect upon non-pneumatic equipment.

The definition of different forms of tires adopted for the purpose of regulations has evidently presented some difficulty. The pneumatic tire differs so widely from the solid tire that this difference is wide enough in the majority of cases to preclude the necessity for precise definition. The introduction, however, of a third class of tire described as a cushion tire has brought about some difficulty. Cushion tires of the type referred to generally depend for their extra cushioning as compared with solid tires upon the design of the tire allowing additional opportunities for displacement of the rubber under load. This is usually obtained by moulding various patterns of tread having the appearance of grooves in the tire. In similar manner the sides of the tires, either in combination with tread grooves or not, are arranged with a series of cavities.

In some popular forms the extra displacement is permitted by the presence of a circumferential chamber in the interior of the tire, and attempts are often made, presumably as a matter of selling propaganda, to get such tires regarded as pneumatic tires, whereas it is clear that the tire is not pneumatic in any proper sense—*i. e.*, it does not depend upon the presence of air for its cushioning capacity.

Quite logically, cushion tires of this kind should be treated advantageously as compared with solid tires, and in certain countries, notably the Scandinavian countries, this is done by means of an elaborate system of tests directed toward finding a figure representing the cushioning capacity and governing the maximum load at which such tires can be used.

Except for this variety of tire, which has undoubtedly served a useful intermediate purpose between the solid and the pneumatic, the classification of tires into the two headings—pneumatic and non-pneumatic—is fairly clearly shown by the legal definition of a pneumatic tire used for legislative purposes in Great Britain. This states in effect that a "pneumatic tire is a tire which is provided

with a continuous closed chamber containing air substantially above atmospheric pressure which is capable of inflation or deflation by the driver without removal from the wheel or vehicle and collapses when deflated and subjected to normal load."

### Standardization

The general application of the word "standardization" in the tire industry is in respect to dimensions only and not to quality, materials, or design. The only points of measurement which are definitely governed by standardization arrangements in respect to tires are those which are required to ensure that tires are a proper fit on the rims for which they are intended, and that by this means tires bearing the same size descriptions shall be interchangeable on their correct rims all over the world, irrespective of different makes.

This standardization, however, does not apply to the tires themselves, and, as far as is known, there is no country in the world which provides any standardization of the actual sizes of the tires.

The dimensions which govern the tire industry are those standardized for the portion of the motor industry manufacturing rims and wheels and granting that the rim dimensions are standardized in all essential features, accepted, and worked to by all manufacturers, the tire maker has no difficulty in providing essential dimensions of his tire in such a way that an accurate and interchangeable fit is ensured.

The main work in connection with the provision and issue of standards from time to time is done in England by the Society of Motor Manufacturers and Traders which has a special Standards Department charged with the sole duty of formulating, agreeing, and issuing standard dimensions in conjunction with all the industries affected. In the United States a similar duty is performed by the Tire and Rim Association of America, Inc.

In selecting and formulating British Standards, the closest regard is always given to the United States standards in view of the dominating position held by America in the motor car industry, and as a matter of fact the rim standards for giant pneumatic tires used by both countries are identical.

Details of the standardized rim dimensions issued in Great Britain, which also correspond for all practical purposes with U. S. A. Standards, are shown in the Institution of Automobile Engineers' Data Sheets, Nos. 148 and 149, dated March, 1928.

Commenting upon these standards, they only provide for rims taking the wired type of tire known in the United States, also under the name of the "Straight-side" tire. Tires having this type of attachment have now practically eliminated all other forms of attachment as the original equipment of vehicles in all the world's manufacturing countries.

Also, only the interior contour is provided for, the exterior shape, including the method of attachment of rim to wheel being left to the requirements of individual design. The shape and dimensions of the interior contour are those which mainly affect the accuracy of the tire fit.

In diameters, the principle is accepted that diameters shall only move in steps of even or complete inches—i. e., there shall be no fractions of an inch.

In practice the present needs of heavier transport are satisfied by a very limited range of rim diameters, applied to a similarly limited range of rim widths.

The rim diameters of 20 in., 22 in., and 24 in. have now almost universal acceptance in all motor manufacturing countries.

In respect of rim sections, these are described by a figure indicating, not the

rim widths, but the nominal widths of the tires which are intended for them: 5 in., 6 in., 7 in., 8 in., 10 in.

Thus each diameter made in each section would provide 15 different rims, each with one or two different nominal sizes of tire to fit.

Reference has already been made to the fact that provided that a tire is a correct fit for a rim made to standard dimensions, all the other tire dimensions are not standardized. It follows that two different makes of tires are not necessarily of the same dimensions, even though they bear the same size marking. That is why the tire size is always described as "nominal."

There is, however, a certain conventional practice followed in the relation between the tire size *marking* or description and the actual diameter of the rim. Twice the nominal tire section, plus the rim diameter, is equal to the nominal tire diameter. Thus, if a tire nominally 6 in. wide is put upon a rim 20 in. in diameter, the overall diameter is nominally 6 in. by 2 plus 20 in. = 32 in., and the tire would be described as 32 by 6.

In the broad sense, the actual tire dimensions adopted by different tire makers have not varied sufficiently to cause any inconvenience, but of late attempts to improve the service capacity of tires have led some makers to diverge so widely from common practice that difficulties are being encountered. Attempts are therefore being made to set some limits to the amount of divergence from the nominal which may be permitted, this being for the present nominal size plus approximately 10 per cent., *i. e.*, a 6-in. tire may measure 6.6 in., a 7-in. tire may measure 7.7 in., an 8-in. tire may measure 8.8 in., etc.

Obviously the actual tire size has an important bearing upon the wheels and the spacing when dual tires are used.

# The Coefficients of Friction between Rubber and Various Materials

## Part II—Gripping Friction of Rubber Belting

R. Ariano<sup>1</sup>

### 1. Method of Test

A length of belting was placed over a cast iron pulley 16 in. in diameter; one end, carrying a pan for weights, was allowed to hang freely, while the other end was fixed to a spiral spring attached to a vertical frame behind the pulley. By altering the point of attachment of the spring the belt could be made to contact with the pulley over an arc ( $\theta$ ) varying from  $50^\circ$  to  $203^\circ$ . A scale laid along the spring enabled the tension ( $T_2$ ) in the fixed end of the belt to be measured, the tension ( $T_1$ ) in the free end being equal to the applied load. It was found that  $T_2$  always bore a linear relationship to  $T_1$ , so that the coefficient of friction ( $f$ ) could be calculated from the equation:

$$T_2 = T_1 e^{f\theta} \dots \dots \dots (1)$$

Except where otherwise stated, precautions were taken to minimize slippage of the belt over the pulley.

### 2. Results of Tests

The belts, before testing, were rubbed vigorously with a rag to bring the surface into normal service condition. The results in Table I represent the mean for 5 values of  $\theta$ ; the figures for the individual tests did not differ from the mean by more than  $\pm 0.015$ , showing that equation (1) holds good for rubber-fabric belting. To determine the friction on materials other than cast iron, the pulley face was covered with a strip of the material in question.

TABLE I  
COEFFICIENT OF FRICTION ( $f$ ) OF BELTING

Belts covered with rubber A:	2-Ply	3-Ply	4-Ply
On cast iron.....	0.264	0.264	0.263
On iron.....	0.279	0.268	0.261
On wood (walnut).....	0.286	0.279	0.272
On rubber*	0.34	0.32	0.296
Belts covered with rubber L:			
On cast iron.....	0.39	0.51	0.36
On iron.....	0.365	0.422	...
On wood.....	0.367	0.423	...
On rubber.....	0.394	0.484	...

\* Much harder quality than A and L.

The following values of  $f$  were obtained with two leather belts 4 mm. thick:

	35 Mm. Wide	40 Mm. Wide
On cast iron.....	0.102	0.09
On iron.....	0.116	..
On wood.....	0.177	..
On rubber.....	0.25	..

<sup>1</sup> From *Il Politecnico*, 1929, Nos. 10-11; for Part I see *Ibid.*, 1929, No. 5; *India Rubber J.*, 78, 351 (1929).



With leather belting the friction was influenced by the nature of the material forming the pulley surface much more than was the case with rubber belting. With the latter, however, the friction varied considerably according to the type of rubber used, and with rubber A the friction was substantially independent of the number of plies, whereas with L it varied markedly. As it seemed possible that this variation might be due to differences in the condition of the rubber surface, the effect of treating the surface in various ways was tried (see Table II).

TABLE II  
COEFFICIENT OF FRICTION ON CAST IRON (BELTING COVERED WITH RUBBER Z)

	4-Ply Belt	3-Ply Belt
(1) One month after manufacture.....	0.23	0.22
(2) After 48 hours' aging at 78° C.....	0.30	..
(3) After one year's shelf aging.....	..	0.21
(4) As (3) but surface scored with scratches 1 cm. apart and at 45° to the belt edge.....	0.31	0.24
(5) After wiping with a rag dipped in benzine.....	0.38	0.44
(6) Rubbed lightly with emery cloth.....	..	0.55
(7) Rubbed with emery cloth and wiped with benzine..	..	0.67
(8) As (7) but surface scored as in (4) with cuts 3 mm. deep.....	..	0.52

The following conclusions are drawn from these results:

(I) Aging did not greatly affect the friction.

(II) Removing the surface film by emery or benzine considerably increased the friction, a result confirmed by other tests. This was probably due to the removal of bloom, resin, etc., since in another test rubbing off the sulfur bloom increased the friction from 0.257 to 0.537. In other experiments dusting the surface with talc lowered the friction from 0.264 to 0.124; wetting the belt with water had no effect.

(III) Slight incisions in the surface somewhat increased the friction; this cannot have been due to any change in the distribution of deformations in the rubber (because deeper incisions tended to lower the friction), but must be ascribed to breaking the continuity of the surface, which may have been contaminated with bloom, resin, etc. (*cf.* effect of removing these substances).

(IV) The results confirm a previous observation that deep incisions (cavities) in a tire tread lower the friction. This may be due to the increased ease of deformation; it cannot be ascribed directly to the presence of air pockets, because tests on a pulley with cavities in its surface showed that these did not lower the friction.

### 3. Coefficient of Friction and Velocity of Slip

In the above experiments the friction coefficients were much lower than those obtained by other workers (*e. g.*, 0.28 to 0.8 for leather on iron). These latter high values, however, were obtained at a comparatively large velocity of slip, whereas the author's tests were made at practically zero velocity; and it is known that the friction is greatly influenced by changes in this velocity.

Experiments were therefore made to see how the friction coefficient was affected by letting the belt slip over the pulley. This was done by interposing a strip of soft rubber between the fixed end of the belt and the spring; the loading pan was held while the weights were placed in it, and then suddenly released. The stretching of the rubber then caused the belt to slip over the pulley with a velocity *v*. The follow-

ing results show that small variations in the velocity of slip may considerably affect the friction, especially with rubber belting:

Leather belting:  $v = 0$ ;  $f = 0.09$   
 $v = 0.7$  cm./sec.;  $f = 0.133$

Rubber belting (4-ply, rubber Z):  
 $v = 0$ ;  $f = 0.25$   
 $v = 0.33$  cm./sec.;  $f = 0.44$

Slip in belts when running might be caused by the difference in tension ( $T_1 - T_2$ ) between the two ends giving rise to a "creep," the rate of which would increase with the deformability of the belt, hence it seemed of interest to determine whether the deformability was related to the friction coefficient. The 2-, 3-, and 4-ply belts with rubber A (see Table I) were found to differ markedly in extensibility and compressibility, but not in friction coefficient, whence it appears that in practice the deformability does not directly influence the friction measured at negligible velocities of slip.

#### 4. Coefficients of Friction for Rubber Belting and Rubber-Tired Wheels

The friction values for belting are considerably lower than those for rubber tires. To elucidate the cause of this difference, strips of belting rubber S 30 mm. wide and of various thicknesses were prepared; these, and the other rubbers used for these tests, were cleaned with emery cloth before testing. Experiments were made also with the rubbers used for solid and pneumatic tires.

TABLE III

	Coefficient of Friction ( $f$ )
Belting rubber S, 1 mm. thick.....	0.708
Belting rubber S, 3 mm. thick.....	0.654
Belting rubber, 10 mm. thick.....	0.512
3-Ply belt made with rubber S.....	0.38
Tire rubber R, 10 mm. thick.....	0.88
Tire rubber B, 10 mm. thick.....	0.61
Tire rubber M, 7 mm. thick.....	0.58
Tire rubber M, with Pirelli tread pattern.....	0.43

The all-rubber strips gave higher figures than the rubber-fabric belting. The values for the former were within the range previously found in tests on actual tires, showing that the two types of test give substantially similar results (and incidentally both show the influence of the tread pattern in reducing friction), in spite of the fact that the rubber is flexed in the pulley test, but not in the test applied to tires.

The velocity of slip for an all-rubber belt was found to increase rapidly with the applied load, and to be much greater than for a rubber-fabric belt.

It was anticipated that an easily deformable rubber, by giving a high velocity of slip, would show a high friction coefficient, but this was found not to be the case, whence it appears that the dominating factor in determining friction is the condition of the rubber surface.

The increase in friction with velocity of slip may account for the fact that with tires the friction normal to the direction of travel is greater than that in this direction, owing to the greater ease of deformation in the former case. The difference between the friction in the two directions may, however, be less when the vehicle is in motion.

#### 5. Other Determinations of Friction between Rubber and Other Materials

Although, as already stated, the flexing of the belt round the pulley did not appear to affect the friction, further experiments were made to see whether the

shape of the contacting surfaces had any influence on the result. Measurements were therefore made of friction between plane surfaces; a rubber sheet (or portion of a belt) was affixed to a horizontal plate, which was supported on rollers and could be subjected to a variable horizontal force. A sheet of the other material in question (not free to move horizontally) was pressed onto the rubber under a known load ( $N$ ). The horizontal force on the lower plate was increased until the friction was overcome and the plate moved.

The condition of the surface was again found to be an important factor (see Table IV), and the values of the friction coefficient were similar in magnitude to those obtained by working on a pulley.

TABLE IV  
COEFFICIENT OF FRICTION ( $f$ ) OF BELTING AGAINST WOOD

	3-Ply Belt, Rubber S	2-Ply Belt, Rubber A	
	$N = 32$ Kg.	$N = 32$ Kg.	$N = 51$ Kg.
Wiped with benzine.....	0.135	0.26	0.33
Rubbed with fine emery and then wiped with benzine.....	0.38	0.51	0.62

In all the subsequent experiments (Table V) the rubber surface was rubbed smooth before testing; the other surfaces (except where specially smoothed) were what would be termed "smooth" in ordinary technical practice.

TABLE V  
COEFFICIENT OF FRICTION ( $f$ ): TEMPERATURE 15–20° C.

Rubber Surface	Other Surface	Load $N$ in Kg.				
		32	51	76	103	152
2-Ply belt, rubber A.....	Wood	0.51	0.62	0.64	0.66	0.59
4-Ply belt, rubber A.....	Wood	0.72	0.71	0.88	0.85	0.73
4-Ply belt, rubber A.....	Iron	0.66	0.70	0.65	0.73	..
2-Ply belt, rubber L.....	Wood	0.64	0.75	0.74	0.70	0.65
4-Ply belt, rubber L.....	Wood	0.76	0.78	0.83	0.70	0.72
3-Ply belt, rubber S.....	Wood	0.38	0.38	0.41	0.49	0.46
3-Ply belt, rubber S.....	Cement	0.48	0.50	0.54	0.59	0.58
3-Ply belt, rubber S.....	Cement smoothed with emery	0.57	0.58	0.58	..	..
All-rubber belt R.....	Wood	0.55	0.67	0.70	0.77	0.70
All-rubber belt R.....	Cement	0.68	0.67	0.67	0.73	0.68
All-rubber belt R.....	Iron	0.86	0.85	0.85	0.90	..
All-rubber belt R.....	Polished iron	1.10	1.14	1.1	..	..
All-rubber belt B (10 mm. thick)....	Wood	0.33	0.39	0.43	0.47	0.49
All-rubber belt S (10 mm. thick)....	Wood	0.28	0.30	0.35	0.41	0.38
All-rubber belt S (10 mm. thick)....	Cement	0.49	0.51	0.56	0.68	..
All-rubber belt S (10 mm. thick)....	Iron	0.61	0.66	..	..	..
All-rubber belt S (10 mm. thick)....	polished iron	0.82	0.80	0.78	..	..

The following conclusions are drawn from the results in Table V:

(I) The nature of the surface (iron, wood, or cement) and the degree of smoothness of this surface both affect the friction, but the smoothness is the dominant factor, a smooth surface giving high friction; this suggests that the apparent differences between iron, wood, and cement may really be due only to differences in smoothness.

(II) Friction increases with the load ( $N$ ); in some cases there are signs of a maximum.

(III) The friction coefficients for plane surfaces are of the same order of magnitude as those obtained in tests on pulleys, in spite of the fact that in the former case the load  $N$  has a predetermined constant value, whereas in the latter case it increases as  $T_1$  is increased.

As in the previous tests on tires, a pattern cut in the rubber surface lowered the friction (*cf.* following figures for a sheet of rubber with one surface smooth and the other bearing the Pirelli tread pattern):

$N =$	COEFFICIENT OF FRICTION ( $f$ )			
	32 Kg.	51 Kg.	76 Kg.	103 Kg.
Smooth surface.....	0.89	0.88	0.81	0.87
Patterned surface.....	0.79	0.83	0.78	0.81

#### 6. Influence of Tension on Coefficient of Friction

This is of interest because in practice the rubber or belt may be in a state of tension while slipping occurs. Tests were therefore made as in paragraph 5, but using sheets of rubber fixed in a stretched condition to the supporting plate. The following friction coefficients (rubber R against iron surface) were obtained:

$N$	ELONGATION OF THE RUBBER			
	0%	4%	11%	20%
32 kg.....	1.10	0.92	0.92	0.89
51 kg.....	1.14	0.97	0.97	0.97
76 kg.....	1.10	0.97	0.97	0.97
103 kg.....	..	..	0.93	0.93

Beyond a slight decrease with the first 4 per cent. stretch the friction is not affected. This is in accord with the fact that the friction coefficient for pneumatic tires is not influenced by the inflation pressure.

#### 7. Influence of Temperature on Friction

This was examined by heating the iron plate laid on top of the rubber sheet with the following results:

$N$	TEMPERATURE OF PLATE ( $^{\circ}$ C.)			
	40 $^{\circ}$	55 $^{\circ}$	70 $^{\circ}$	82 $^{\circ}$
32 kg.....	0.92	0.58	..	0.58
51 kg.....	0.84	0.59	..	0.58
76 kg.....	0.71	0.56	0.56	0.56
103 kg.....	0.72	0.55	0.57	..

Up to 55 $^{\circ}$  C. the friction falls considerably, but above this it changes little.

#### 8. Transmission of Tractive Force by Belting

In the tests described in paragraph 5 it was found, especially with all-rubber specimens, that the horizontal force was not transmitted to the far end of the specimen until it reached a certain limiting value, *i. e.*, the rubber began to slip first at the end where the force was applied, and the zone of slip lengthened as the force was increased. If the length of this zone is denoted by  $l$  and the horizontal force by  $F$ , the following empirical relationships are found to hold for all-rubber specimens:

$$\text{For a given vertical load (N): } F = F_0(e^{kl} - 1) \dots \dots \dots (2)$$

$$\text{For a given horizontal force (F): } l = \frac{h}{N^m} \dots \dots \dots (3)$$

where  $F_0$ ,  $k$ ,  $h$ , and  $m$  are constants.

When there is slippage only over a part of the specimen this part becomes

stretched and therefore thinner; consequently the load  $N$  is distributed non-uniformly over the specimen, the load per unit area being less on the stretched than on the unstretched part. (Experimental data are given in the original to show the magnitude of this difference.) Using the equations deduced in previous papers for the stress-strain curves of rubber under tension and compression the theoretical distribution of the load is deduced, and a formula is developed giving the horizontal tension at any part of the specimen and also the value of the force ( $F$ ) which just suffices to produce slip along the whole length of the specimen; this formula, however, is too complex for convenient practical use. A further formula is deduced relating  $F$  with the length ( $l$ ) of the zone of slip; this is the theoretical equation corresponding to the empirically deduced equation (2), and is found to be analogous in form to the latter.

### 9. Variation of Pressure Normal to the Pulley Surface

In the method described in paragraph 1 the pressure which the belt exerts on the pulley surface varies because the tension in the belt changes along its length, and in deriving formula (1) it is assumed that the coefficient of friction is independent of this pressure. The distribution of pressure was examined by boring holes through the pulley face and connecting these to a compressed air supply; the belt pressure was then measured by determining the air pressure which just lifted the belt off the pulley.

In a belt passing over a fixed pulley, with both ends hanging free, one end carrying a heavier load ( $T_1$ ) than the other ( $T_2$ ), the pressure exerted by the belt was found to decrease in passing from the heavily loaded toward the lightly loaded end, the rate of decrease being greatest at the former and very small at the latter end. (The results are shown in graphs in the original.)

If  $T_2$  equals zero,  $T_1$  must reach a certain limiting value  $T_0$  before the belt slips; consequently, equation (1) should more accurately be written:

$$T_1 = T_2 e^{f\theta} + T_0 \dots \dots \dots (4)$$

By plotting  $T_1$  against  $T_2$  the value of  $T_0$  was calculated (see Table VI).

TABLE VI

	$\theta$	$T_0$ (in Kg.)	$f$
Leather belt, 40 mm. wide.....	149°	9	0.09
Ditto.....	184°	10	0.096
All-rubber belt S, 50 mm. wide.....	86°	0.30	0.26
Ditto, rubbed with emery.....	86°	3.4	0.54
Rubber-fabric belt A, 50 mm. wide.....	59°	4.6	...
Ditto.....	93°	9.4	...
Ditto.....	149°	14.8	...
Ditto.....	183°	18	...
Ditto.....	203°	20	...
Rubber-fabric belt Z, 50 mm. wide:			
Cleaned with rag.....	149°	8	0.21
Cleaned with emery.....	149°	52	0.41
Cleaned with emery and benzine.....	149°	89	0.55
Cleaned with emery and benzine and surface finely scored.....	149°	102	0.67

It will be seen that  $T_0$  increases with the arc of contact ( $\theta$ ) and with the coefficient of friction ( $f$ ). Increasing the pressure exerted by the belt, *e. g.*, by loading it with sheet lead, increases the value of  $T_0$ :

	Not Cleaned	Cleaned with Emery and Benzine
Without loading.....	1.50 kg.	17.0 kg.
Loaded with 5.65 kg.....	5.27 kg.	30.6 kg.

In a concluding note the author comments on a recent publication by Agg ("Tractive Resistance of Automobiles and Coefficients of Friction of Pneumatic Tires," Bulletin 88 of Iowa State College), pointing out, and in part explaining, the differences between his own results and those of Agg.



## Factors in the Works Control of Plasticity by the Williams Method

T. L. Garner<sup>1</sup>

Two methods are available for the measurement of plasticity in the works—the Williams and the extrusion method. Generally, when the former is used, the original method is modified in some way, the following being used in this case. The plastometer, with a long handle so that it can be operated through a hole in the roof of the oven without opening the oven door, is used with a loose die, the size being varied according to plasticity, but for routine testing of masticated rubber a  $\frac{3}{4}$ -in. disc  $\frac{1}{4}$  in. thick is used. The sample of rubber used is rather less than  $\frac{1}{4}$  in. in thickness to prevent the rubber creeping round the die and touching the top plate when the die is pressed into it; the size of test piece is about  $1\frac{1}{2}$  in. square. The samples are cut off masticated rubber plied up to give a thickness of about  $1\frac{1}{2}$  in.

Each morning the plastometer is set so that when resting on the steel die alone a reading of 400-thousandths of an inch is shown. This means that with the die on a sample of rubber, no indication is given on the plastometer gage until the thickness of rubber between the bottom plate and the die is 400-thousandths of an inch, *i. e.*, a constant thickness in each case. As soon as this is reached, and the gage hand moves, a stop watch is begun and the time taken for the hand to cover 50 divisions on the gage is taken as the plasticity figure. An agreement can be obtained under ordinary working conditions of about ten seconds, and the test does not require skilled control.

The above brief description is recorded to give some idea of the method used in obtaining the results given below, and is a bare outline only of the procedure. Fuller details are available of similar methods in the literature on the subject (*e. g.*, de Visser, *Calender Grain*).

During the routine testing, discrepant results were obtained for which no satisfactory explanation was obtainable at first, but which were eventually shown to be due to the smearing of French chalk over the surface of the rubber for test. In view of the importance of the fact that the presence of chalk on the surface of the rubber completely vitiated the value of the test, it was considered of interest to record the results obtained with various other powders, and that is the object of this short paper. So far as the writer is aware no previous reference has been made to this subject.

The following table shows the results obtained with a wide range of different powders rubbed on to the surface of the sample immediately before test. It was found that duplication was generally as accurate as with clean masticated rubber, showing that no special precaution was necessary as to the amount of powder spread on to the rubber except to see that the area was completely covered. In a few cases, however, readings were affected by the time the sample was in the oven; this is contrary to experience with clean masticated rubber.

From these results it will be seen that the presence of French chalk on the surface of the rubber reduces the plasticity number by almost one-half, and the effect of a substance such as stearic acid, which melts under test, is very slight. There

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is also no relation between particle size and the plasticity number, for the particles of colloidal zinc oxide have the same effect as those of ordinary zinc oxide, and lithopone has yet a different effect. Carbon blacks show one of the few instances of an increase in the plasticity number. A remarkable reduction in the plasticity number is shown when samples are dusted with some of the accelerators in common use, and also with lime and graphite; sulfur has no effect.

Compound on Surface of Rubber	Plasticity (Secs.)	Compound on Surface	Plasticity (Secs.)	Compound on Surface	Plasticity (Secs.)
Clean	154	Kieselguhr	83	Vegetable black	96
French chalk	85	Sulfur	151	Graphite	19
Zinc stearate	86	Lithopone	142	"Thermatomic" black	142
Zinc oxide (ordinary)	164	China clay	112	"Micronex" black	182
Zinc oxide (colloidal)	166	Litharge	126	Diphenylguanidine	18
Light calcined magnesia	157	Lime	47	Triphenylguanidine	118
Heavy calcined magnesia	179	Red oxide	154	Di-o-tolylguanidine	34
Magnesium carbonate	117	Titanium white	117	Tetraethylthiuram-disulfide	36
Barytes	140	Carbon black	180	Stearic acid	136

The results may be explained by an analogy to the piston. The normal action of the latter is that of a ram driving a wedge of material into the solid, but this is so only if the metal sticks to the solid (Fig. 1). If, however, the solid can flow over the surface as when graphite is present the wedge action is less. In other

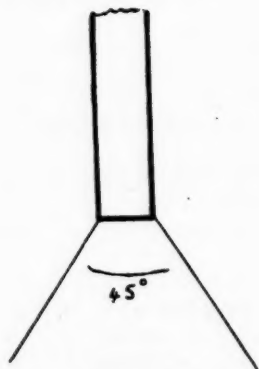


Figure 1



Figure 2

words, there is less material moved if friction between the two surfaces is diminished, *i. e.*, less work is done (Fig. 2), and the better a substance is as a lubricant between steel and rubber, the lower will be the plasticity number; this affords a measure of the lubricating effect of the powder under test.

As has been shown, the majority of powders used in the rubber industry have an effect upon the plasticity number, in some cases enormous, and it is essential in using a method of this kind that any contamination is avoided. Further work on this subject is being carried out, as a matter of interest, using dies of different materials. The die used in the above was steel, unpolished.

The fact that it is possible to obtain a higher value than that for clean rubber, by the use of suitable powders, shows that some slipping occurs with clean rubber and an exact mathematical interpretation of the plasticity figures is not possible.

## A Simplified Goodrich Plastometer<sup>1</sup>

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A simplified form of the Goodrich plastometer, for factory-control use, is described and its use in measuring plasticity is discussed. This is accomplished by measuring the softness and the retentivity of the rubber, since plasticity has been shown to be made up of these two factors.

**I**N RECENT papers a new definition of plasticity (2) was set forth and a power-driven plastometer (3) for measuring the plasticity of rubber was described. Some preliminary data with this plastometer have also been recorded (1). From this definition the plasticity of a body is measured by its susceptibility to and retentivity of deformation; that is, plasticity is made up of two factors—softness and retentivity. Expressed in equation form

$$\text{Plasticity} \equiv \text{softness} \times \text{retentivity} \quad (1)$$

This power plastometer has now been simplified for factory control.

### Essential Parts of Instrument

A schematic drawing of the simplified plastometer is shown in Figure 1. It consists essentially of the following parts: the frame, *A*; a circular lower plate, *B*, on which the cylindrical rubber test piece rests; an upper loading plate, *C*, connected by a thin rod, *D*, to a specially constructed dial gage, *G*; the hollow rod, *E*, which slides between the guides, *F*, carries the weight, *W*; the rod, *E*, rests on the loading plate, *C*, when the lever, *L*, held by the catch *H*, is lowered; the plates, *B* and *C*, are of the same

<sup>1</sup> Received October 7, 1929. Presented before the meeting of the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, N. J., September 26 to 28, 1929.

area as the test piece, 1 sq. cm. (0.155 sq. in.); the weight,  $W$ , is adjusted so that the net load on the test piece after correcting for the effect of friction is 907 grams (2 lbs.) The gage has a 10-cm. (4-in.) diameter dial, subdivided to 0.0127 cm. (0.005 in.) with 1 revolution for 1.27-cm. (0.5-in.) travel. Bulky parts of the gage, stem and cross arm, are hollowed out to decrease the load on the test piece during recovery. The combined load of the upper plate, connecting rod, and effective weight of the gage is about 35 grams (0.077 lb.). The effect of friction is about 10 grams (0.022 lb.).

The first reading taken is the initial height, the distance between the upper and lower plates with the sample inserted under the pressure of the gage spring and weight of the loading plate and rod only. The load is applied to the test piece for a definite time, during which any decrease in its height may be read from the gage at any moment. After the load is removed by raising the lever,  $L$ , the upper plate remains in contact with the test piece and the recovery after any interval may also be read from the gage. The softness and retentivity are calculated from the dial readings at the end of the compression and recovery periods.

A furnace surrounding the test piece maintains it at the desired temperature. The outside shell of the furnace, 1, is cylindrical, about 15 cm. (6 in.) in diameter and 20 cm. (8 in.) high, made of galvanized steel 0.071 cm. (0.028 in.) thick, lined with asbestos 0.48 cm. (0.19 in.) thick. The shell is equipped with a door, 2, about 13 cm. (5 in.) wide and 19 cm. (7.5 in.) high, to allow access to the inside of the shell. An aperture, 3,  $4.5 \times 4.5$  cm. ( $1.75 \times 1.75$  in.) through this door permits the insertion of test pieces into the heating chamber for preheating and testing. Tweezers are used to charge and discharge samples through this aperture, which is small to avoid large temperature disturbances.

The heating chamber, about 5 cm. (2 in.) in diameter and 7 cm. (2.75 in.) high, is constructed of 0.071-cm. (0.028-in.) sheet steel and has a 0.48-cm. (0.19-in.) transite-board top and bottom, 4 and 5. The resistance coil, 6, 0.32 cm. (0.125 in.) in diameter is made of about 550 cm. (18 ft.) of 0.032-cm. (0.0125-in.) diameter nichrome wire laced between the transite-board top and a transite-board ring, 7, with terminals for connection to a 110-volt circuit. A flashlight bulb, 8, (3.5 volts) illuminates the heating chamber only when the aperture is opened.

The temperature, read on the mercury thermometer, 9, with the bulb near the test piece, is controlled with a thermostat. Temperatures up to  $150^{\circ}\text{C}$ . can be maintained with a variation of not more than  $1^{\circ}\text{C}$ . at any given spot. In the horizontal plane of the test pieces there may be a maximum variation of not more than  $3^{\circ}\text{C}$ . Vertically, there may be a gradient of  $3^{\circ}$  to  $4^{\circ}\text{C}$ . per centimeter. Opening the aper-

ture  $1\frac{1}{2}$  minute out of every  $2\frac{1}{2}$  minutes causes a maximum variation of temperature at center of the oven of  $2^{\circ}\text{C}$ .

### Preparation of Test Pieces

The standard test piece is a right circular cylinder 1 sq. cm. (0.155 sq. in.) in cross-section area and 1.13 cm. (0.444 in.) high (height = diameter). To cut this test piece a special cutting machine (Figure 2) has been developed. A motor, 1, is equipped with a hollow extension shaft, 2, running

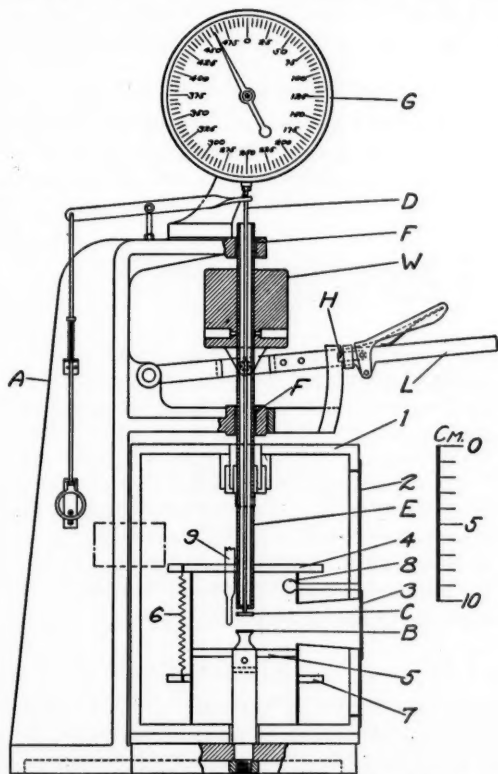


Figure 1—Front View of the Simplified Goodrich Plastometer. Sectioned in Part and Furnace Turned through 90 Degrees

through the thrust ball-bearing, 3, and provided at its end with a conical entrance to receive the cutting and trimming accessories, 4 and 5. The cutting tool is a thin tube of tool steel with a conical shank. The sample of rubber from which the test piece is to be cut is held against the sharp edge of the cutter, lubricated with soap solution, and backed with a piece of soft rubber. The test piece is ejected from the cutter by means of the ram rod, 6, the motion of which is effected by operation of a lever, 7. The holder for trimming, 5, con-

sists of a tube with a conical shank to fit the shaft of the motor, with a portion of its length hinged, 8, to facilitate the insertion and removal of the test pieces. The cylindrical clamp, with the test piece inserted, is then pushed into the motor axis and a lubricated, sharp, thin-edged knife, such as a razor blade, is gently held against the end of the holder and pressed into the rubber as the test piece rotates. After one end has been trimmed in this fashion, the adjusting block, 9, in the holder is set to give the proper length. To keep the test piece from slipping in the holder as the trimming knife is pressed against it, needle points, 10, or a spring, are provided. The test piece is washed with water and dusted with soapstone.

#### Method of Procedure

Compression and recovery periods of 30 seconds have been adopted for rubber testing. These are read from a stopwatch or large-dial Telechron clock with a second hand.

The softness, expressed in terms of the change in height, is

$$S = f(t, F) \frac{h_0 - h_1}{\frac{h_0 + h_1}{2}} = K \frac{h_0 - h_1}{h_0 + h_1} \quad (2)$$

where  $F$  is the applied load,  $h_0$  is the initial height of test piece,  $h_1$  is the height after 30 seconds' compression,  $h_0 - h_1$  is the total amount of deformation in time,  $t$ . As a first approximation  $(h_0 + h_1)/2$  is taken as the average height during deformation. The exact form of  $f(t, F)$  is not yet known. The load and time are constant, and it is assumed that the variation in  $f(t, F)$  for various stocks is such that any changes in  $t$  or  $F$  will not cause serious inversions in the order of rating them. For the time being, then, relative values for the softness factor may be set up by ignoring variations in  $K$ , so that  $S$  may be taken as

$$S = \frac{h_0 - h_1}{h_0 + h_1} \quad (3)$$

Retentivity is defined as the ratio of the amount of deformation retained to the amount of deformation given, and may also be expressed in terms of the height of the test piece, as

$$R = \frac{h_0 - h_2}{h_0 - h_1} \quad (4)$$

where  $h_2$  is the height after 30 seconds' recovery.

Plasticity then is

$$P = S \times R = \frac{h_0 - h_2}{h_0 + h_1} \quad (5)$$

From these formulas the range of softness, retentivity, and plasticity is from 0 to 1 for all materials. By setting up standards for unit softness and unit retentivity the results may be expressed as absolute values, but for control work relative values are sufficient.



The temperature at which tests are made should be chosen with due regard to the nature of the material, and to the questions which the data obtained are intended to answer. If 100° C. is adopted, preheating for about 20 minutes is necessary. With this heating time and allowing about 2 minutes for each test, it is desirable to have ten test pieces in the oven at all times.

### Typical Results

The softness, retentivity, and plasticity at 100° C. of pale crepe and smoked sheets, masticated for various times on a 24-in. (60-cm.) mill in batches of 5 and 6 lbs., (2.3 and 2.7 kg.) and on 60- and 84-in. (152- and 213-cm.) mills in batches of 60 and 200 lbs. (27 and 91 kg.), respectively, are shown in

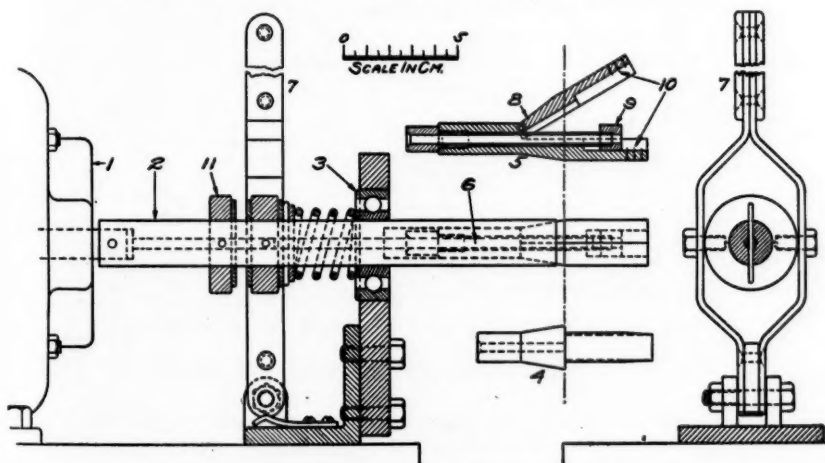


Figure 2—Device for Cutting and Trimming Test Pieces

Figure 3. In these cases 50 minutes on the 60- and 84-in. (152- and 213-cm.) mills is equivalent to about 7 and 5 minutes, respectively, on the 24-in. (60-cm.) mill. The greater irregularity of the data for the larger mills may be attributed to difficulties in sampling and timing. Similar data on some typical compounded stocks are given in Table I.

*Note*—In this article the writers are not reporting characteristics of a rubber stock, but are showing that the instrument described may be used on any rubber stocks. For this reason they are mentioning, in a general way, many stocks. The names of the stocks used, such as the footwear stock, tread stock, reclaim, solid tire, pure gum, and master batches, are intended to be names for groups of rubber compounds which cover a great very range of types that are actually used in the rubber industry.

How these factors change with temperature for smoked sheets and footwear stocks is shown in Figure 4. Table II shows the magnitude of the variations of plasticity in absolute values (columns 2 and 5) and as a temperature coefficient, referred both to the plasticity at 40° C.—i. e.,

$dP/dT/P_{40}$  (columns 3 and 6)—and to the plasticity at the temperature considered—i. e.,  $dP/dT/P_T$  (columns 4 and 7). The variation in plasticity with temperature is higher for stocks of higher plasticity, and for each stock the absolute change in plasticity increases with temperature. The abrupt decrease in the slopes of the plasticity and softness curves and especially of the retentivity curve for footwear stock B

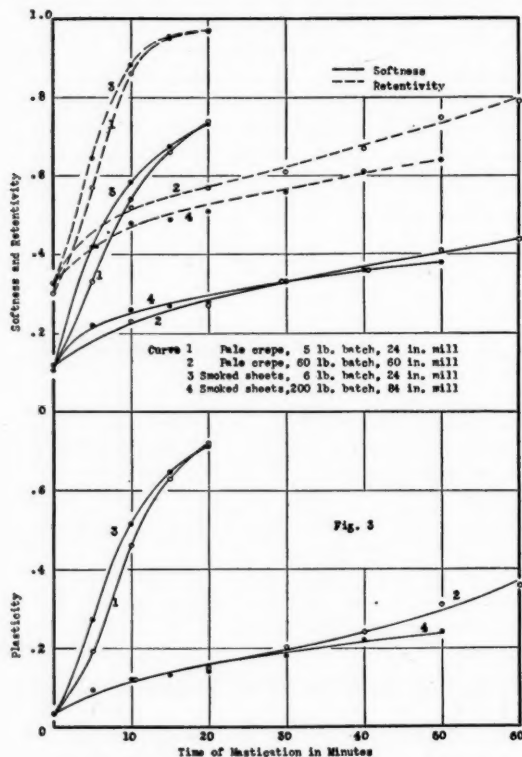


Figure 3—Effect of Mastication upon Plasticity, Retentivity, and Softness Factor of Pale Crepe and Smoked Sheets

near 70° C., indicates that the test pieces were cured during preheating. This suggests that the instrument may be useful in the study of scorching of stocks.

Table I—Plasticity of Various Stocks

SAMPLE	TEMP. ° C.	SOFTNESS	RETENTIVITY	PLASTICITY
Solid tire tread	100	0.23	0.51	0.12
Pneumatic tire tread A	100	0.43	0.73	0.31
Pneumatic tire tread B	100	0.49	0.80	0.39
Pneumatic tire tread C	100	0.52	0.84	0.44
Inner tube stock	70	0.32	0.55	0.18
Reclaim stock A	100	0.07	0.12	0.009
Reclaim stock B	100	0.27	0.17	0.045
Reclaim stock C	100	0.47	0.32	0.15

Table II—Variation of Plasticity with Temperature

SAMPLE	At 40° C.			At 100° C.		
	Change per ° C.	Temp. coef. (1) (2)		Change per ° C.	Temp. coef. (1) (2)	
Smoked sheet, crude	0.0002	0.010	0.010	0.0007	0.035	0.014
Smoked sheet, masti- cated 15 minutes	0.0007	0.026	0.026	0.003	0.11	0.027
Smoked sheet, masti- cated 50 minutes	0.0012	0.024	0.024	0.0055	0.11	0.024
Footwear stock A	0.0017	0.034	0.034	0.009	0.225	0.041
Footwear stock B	0.0015	0.028	0.028	-0.0008	-0.019	-0.004

There is, in general, no correlation between softness and retentivity; i. e., stocks may have high retentivity and low softness or low retentivity and high softness, etc. Data comparing these two factors for tests of about two hundred samples of twenty-eight different stocks are shown in Figure 5. For crude rubber or similar stocks there is some correlation; i. e., stocks having high softness also have high retentivity and, within about the limits of experimental error, retentivity is a single-valued function of the softness. The smooth curve was drawn as the best fit for all the uncompounded rubber. Some of the compounded stocks fall on or near the curve, while others, such as the reclaims, some tread stocks, gas-black master batches, footwear stocks, and heavily loaded clay stocks, clearly do not. More recently it has been found that low grades of rubber do not follow the curve here, but depart more like the reclaimed stocks.

Each of the above results is the average for two or more test pieces of size  $1.1 \times 1.1$  cm. (0.433 in.).

#### Effects of Deviations from Standard Conditions

The quantitative effect produced by definite deviations from standard conditions is important in determining the amount of error to be expected from such accidental deviations as may occur in practice, as well as in determining the effect of choice of standard conditions upon the relative order of rating stocks. The conditions which may be varied, either at will or accidentally, are size and shape of the test piece, the load during compression and recovery, time of compression and recovery, and lubrication of the test piece.

Both softness and retentivity factors may be expected to vary with the dimensions of the test piece. A few observations indicate that the effect of change in height is small, a change of 10 per cent either way from the standard height causing a change in the plasticity figure of only about 3 per cent. A change of 1 per cent either way from the standard diameter causes a change of about 1 per cent in the plasticity figure. By changing the diameter of the test piece and at the same time varying the size of the plates and the load, correspondingly keeping the pressure constant, the plasticity is found to be independent of the area.

Plasticity,  $P$ , appears to vary as some power,  $n$ , of the load,  $L$ ;  $P = \text{constant} \times L^n$ , where  $n$ , however, differs little from unity for the range 500 to 1350 grams.

The interval (30 seconds) for compression and recovery

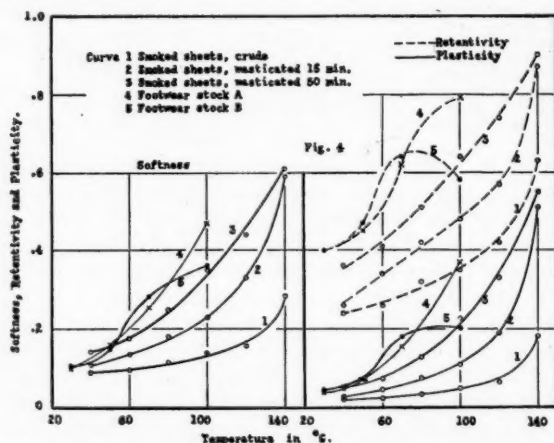


Figure 4—Variation of Plasticity, Retentivity, and Softness Factor with Temperature

was chosen entirely from the standpoint of practical operation. It chanced that recovery is well under way within this period, while the deformation determining the softness factor may or may not be undergoing large changes in rate.

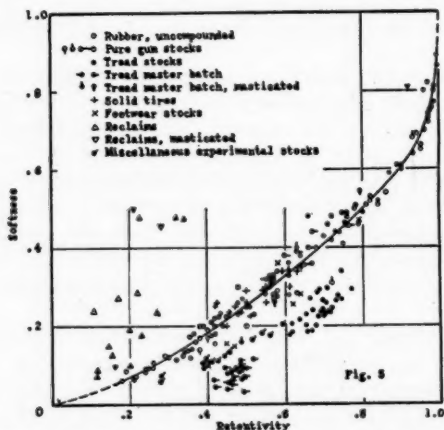


Figure 5—Relation between Softness Factor and Retentivity for Several Types of Rubber Stocks

What practical importance these latter changes may have in classifying and controlling any given species of materials remains to be determined. When it is known, the necessary adaptation in the time interval and in technic should be made.

To determine the effect of lubrication between test piece and the plates, tests were made: (1) with bare plates; (2) with paper between the test piece and plates; (3) with soapstone; and (4) with Nujol on the bearing faces of test piece. Results with the last two were about 6 and 20 per cent higher for crude rubber, dead-milled and unmasticated, and 13 per cent higher for tread stock.

Plasticity both at 40° and 100° C. (Table II, columns 4 and 7) may change from 1 to 4 per cent per degree Centigrade, showing that the testing temperatures must be accurately controlled.

Considering the non-uniformity of rubber it is not necessary for production control to correct for the effects of all these factors. In routine procedure results agreeing within 5 per cent may be expected.

### General Discussion

Other formulas for the softness factor, assuming in each case the elements of load and time constant, have been considered, such as  $\log h_0/h_1$ ,  $(h_0 - h_1)/h_0$ ,  $(h_0 - h_1)/h_1$ . Permanent set, defined as  $h_0 - h_2$ , has been considered as well as retentivity. The eight resulting expressions for plasticity give practically the same relative values. From theoretical considerations, retentivity and  $\log h_0/h_1$  or  $(h_0 - h_1)/(h_0 + h_1)_2$  are preferable. Of the latter  $(h_0 - h_1)/(h_0 + h_1)_2$  appears somewhat simpler.

Only a few data have accumulated from which one might infer what the relationship is between the relative results obtained with the simplified and power plastometers. These indicate that a simple, smooth curve relationship may hold.

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# Thermodynamics of Stressed Vulcanized Rubber<sup>1</sup>

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The first and second laws of thermodynamics are applied to the stretching of vulcanized gum rubber stocks.

Equilibrium stress-strain curves without appreciable hysteresis are described.

The modulus of elasticity of vulcanized rubber for higher elongations obtained from the equilibrium stress-strain curve is capable of giving agreement with predictions of the second law of thermodynamics and the Joule heat effect.

The modulus of elasticity from the equilibrium stress-strain curve is practically independent of the time of cure for a range of cures for elongations less than 600 per cent. The customary stress-strain curves show the rubber to be stiffer with increased cure.

These facts are additional evidence that the important effect caused by vulcanization is a greater resistance to plastic flow or permanent set.

IT IS the purpose of this paper to describe a method of obtaining equilibrium stress-strain curves of vulcanized rubber without hysteresis and to develop the thermodynamics of stressed rubber by beginning with the statements of the first and second laws of thermodynamics.

The thermal behavior of rubber when stretched has been the subject of discussion for many years. In a summary of the early work, Whitby (15) stated that Gough (3) as long ago as 1805 recognized that stretching increased the tem-

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perature of rubber and that a strip of rubber, if extended vertically by means of a weight attached to the lower end, became shorter when heated and longer when cooled. Later Joule (6) independently stated that the stretching of rubber at sufficient elongations increased its temperature, but that at lower elongations the temperature decreased. Lord Kelvin predicted, on theoretical grounds, that stretched rubber would contract on being heated. Joule (6) confirmed this prediction experimentally and made a series of quantitative measurements in regard to the phenomenon. Many later observations and measurements on the effect of temperature on stretched rubber have contradicted those of Gough and Joule. Lundal (9), Bouasse (1), Wormeley (17), Hyde (5), Somerville and Cope (12), and Partenheimer (10) have reported observations, principally stress-strain curves, which show that the rubber has a lower modulus of elasticity at higher temperatures. On the other hand, Schmulewitsch (11), Stevens (13), and Williams (16) found that the elastic modulus increases with the temperature. Gibbons (2) has urged on theoretical grounds that if the rubber behaved reversibly, the modulus of elasticity should be higher at higher temperatures if the rubber warms on stretching.

#### Equilibrium Stress-Strain Curves

Van Rossem and van der Meyden (14) have found that permanent set is negligible at ordinary temperatures; only at higher temperatures was this effect noticeable. Williams (16) obtained stress-strain curves at different temperatures with extreme rapidity in order to eliminate plastic effects, with the result that the modulus of elasticity increased with increased temperature. These curves were independent of the time of cure and were cited as evidence that vulcanization affected the plastic properties more than the elastic properties.

If rubber is stretched continuously at customary rates, true equilibrium is not attained. To obtain points on stress-strain curves at constant temperature and without appreciable hysteresis a customary test piece of rubber is extended vertically by means of a weight attached to the lower end and the weight is oscillated up and down by hand ten to twenty times in the neighborhood of an equilibrium position. After the oscillations have subsided the distance between marks of the test piece is noted. With a given weight the length of the rubber is substantially independent of the direction from which equilibrium was approached and also of the length of time which the weight was allowed to hang. If many measurements are made on a sample that has been died out, the corners crack and decrease the true cross section. This effect is particularly noticeable at elongations greater than 500 per cent. A molded or latex sample, which has not been died out, may be more satisfactory.

Doctor M. Mooney, of this laboratory, has found that vibrating the rubber like a piano wire is as effective as oscilla-

tion in obtaining the equilibrium stress-strain curve. The vibration was produced by repeatedly striking the rubber. Data obtained by him are given in Table I and Figure 1. The rubber was cured at 45 pounds steam pressure or 145° C. for 30, 45, 75, and 90 minutes in a platen press. The composition was: rubber 100, zinc oxide 5, mineral oil 5, sulfur 3.75, and heptene accelerator 0.5 parts. These samples were approximately 0.1 inch (2.5 mm.) thick and were cut with a die to 0.125 inch (3.185 mm.) in width. Curves II, III, and IV, which are at 20 inches (50.8 cm.) per minute, show the rubber to be stiffer with increasing cure up to 60 minutes. As is customary, only the first cycle was obtained. Only one equilibrium stress-strain curve, I, was plotted, since the curves for different cures are substantially identical up to 600 per cent elongation, when cracking of the corners occurs.

Table I—Equilibrium Stress-Strain Data by Oscillating Method  
LENGTH OF SAMPLES\*

Load:	0	250	500	1000	1500	2000	2500
Grams	0	0.55	1.10	2.20	3.30	4.41	5.51
Pounds							
	Inches	Inches	Inches	Inches	Inches	Inches	Inches
30-MINUTE CURE							
Stretching	1	1.40	2.27	4.65	6.45	6.75	
Retracting	1.02	1.48	2.35	4.70	6.35		
Stretching	1.02	1.48	2.30	4.75	6.55	6.95	7.10
Retracting	1.03	1.50	2.40	4.75	6.60	6.85	
45-MINUTE CURE							
Stretching	1.03	1.44	2.21	4.52	6.40	6.86	7.00
Retracting	1.08	1.52	2.37	4.58	6.80	6.86	
Stretching		1.48	2.31	4.60	6.75	7.05	
Retracting	1.08	1.50	2.38	4.83	6.78		
75-MINUTE CURE							
Stretching	1.00	1.40	2.20	4.18	6.20	6.77	
Retracting	1.03	1.48	2.38	4.45	6.40		
90-MINUTE CURE							
Stretching	1.01	1.43	2.25	4.29	6.30	6.87	
Retracting	1.06	1.50	2.45	4.57	6.42		

\* Lengths of samples are given in inches; for length in centimeters multiply by factor 2.54.

#### Effect of Temperature on Modulus

The effect of temperature on the modulus of elasticity for an inner tube stock of high rubber content as determined by the oscillation method is shown in Table II.

Table II—Effect of Temperature on Modulus of Elasticity by Oscillation Method

TEMPERATURE	DISTANCE BETWEEN MARKS (ORIGINALLY 2.50 CM. APART)				
° C.	Cm.	Cm.	Cm.	Cm.	Cm.
36	7.7		8.0		8.0
10		8.3		8.3	

Thus the modulus of elasticity of this rubber is seen to increase with the temperature, inasmuch as the length is greater at a lower temperature with a constant load.

#### Conventions and Definitions

In thermodynamical treatment the physical state of a sample of rubber must be uniquely determined. The state

of a given sample of unstressed rubber is completely determined if the temperature and pressure, temperature and volume, or pressure and volume are stated. For rubber under uniform tension two additional variables, force and length, will be selected for determining the state of the rubber. For use in the equations of thermodynamics the dimensions of their product must be in work units. It is convenient if the variables give mathematical expressions that are simpler than some other set of variables. Thus, for various reasons, the sets of variables, force per unit area and the logarithm of the length, or tensile product and the logarithm of the length, or force and elongation, or force and fractional elongation are found to be not so satisfactory as force and length.

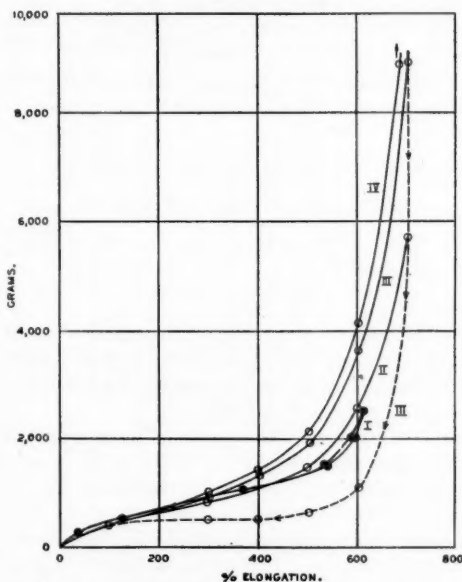


Figure 1—Stress-Strain Curves

- I—Oscillation method for 30-, 45-, 75-, and 90-minute cures
- II—At 20 inches (50.8 cm.) per minute for 30-minute cures
- III—At 20 inches per minute for 45-minute cures
- IV—At 20 inches per minute for 60-minute cures

It will not be necessary to carry all the variables—temperature, pressure, volume, force, and elongation—through all of the mathematical operations. The pressure will be held constant at 1 atmosphere. Consequently, the statement of the temperature of a given piece of unstressed rubber is sufficient to define its state. For a given sample of stressed rubber the statement of the temperature and length or the temperature and force will be sufficient to determine its state, provided there is only one force for any given elongation, or vice versa. As this can only be true if the stress-strain curve has no hysteresis, only equilibrium stress-strain curves will be dis-

cussed. As an example, change of state in stretching 1 gram of vulcanized rubber of 10-cm. length at constant temperature from the unstressed condition to 30-cm. length can be abbreviated, as follows:

1 gram rubber ( $L = 10$  cm.,  $T = 25^\circ$  C.)  $\rightarrow$  1 gram rubber ( $L = 30$  cm.,  $T = 25^\circ$  C.)

#### DEFINITION OF SYMBOLS

$T$	= temperature, degrees Centigrade
$p$	= pressure, dynes per square centimeter
$v$	= volume, cubic centimeters
$f$	= force or tension, grams
$L$	= length, centimeters
$q$	= heat absorbed, calories
$E$	= energy content, calories
$\Delta E$	= increase in energy content, $E_2 - E_1$
$W$	= work done by rubber, $-\int f dL$ calories
$C$	= heat capacity per gram $dq/dT$ , calories per degree Centigrade
$C_L$	= heat capacity per gram at constant length, calories
$A$	= free-energy content, calories
$dA$	= $-dW = f dL$

The numerical results will be expressed in calories.

#### First Law of Thermodynamics

The first law of thermodynamics can be quantitatively stated by the equation:

$$q = \Delta E + W \quad (1)$$

The heat absorbed,  $q$ , by any system is equal to the increase in energy content plus the work done by that system. The first law has no limitations and applies to any system, whether or not the processes are reversible.

*Example 1—Irreversible Retraction, without Doing Work, at Constant Temperature.* If rubber retracts in a calorimeter without doing work it is seen from Equation 1, and from the fact that heat is absorbed, that the energy content of the rubber is greater in the unstressed than in the stressed condition.

1 gram rubber ( $L = 5$  cm.,  $T = 25^\circ$  C.)  $\rightarrow$  1 gram rubber ( $L_0 = 1$  cm.,  $T = 25^\circ$  C.)

By Equation 1,  $q = \Delta E = E_2 - E_1$

The rubber absorbs heat for this change of state and,  $q$  being positive, the energy content,  $E_2$ , of the rubber in the unstressed condition is greater than  $E_1$  in the stressed condition. This should not be confused with potential energy, which is the tendency to do work.

*Example 2—Reversible Retraction at Constant Temperature* Stretched rubber may conceivably retract reversibly, if it is placed in a thermostated testing machine and vibrated or if it retracts according to the equilibrium stress-strain curve.

The change of state is described by the equation:

1 gram rubber ( $L = 5$  cm.,  $T = 25^\circ$  C.)  $\rightarrow$  1 gram rubber ( $L = 1$  cm.,  $T = 25^\circ$  C.)

By Equation 1,  $q = \Delta E + W$

The increase of energy content should be the same as in Example 1, since the rubber is at constant temperature; and the heat absorbed when the rubber does work should be greater by the amount of work done than the heat absorbed when the rubber does no work.

This change of state has an analogy in steam (4) in contact with water when work is done at constant temperature.

1 gram  $\text{H}_2\text{O}$  (liquid) ( $T = 100^\circ \text{C.}$ ) = 1 gram  $\text{H}_2\text{O}$  (gas) ( $T = 100^\circ \text{C.}$ )

By Equation 1,  $q = \Delta E + W$

The work done is the product of the pressure, 1 atmosphere, and  $\Delta V$ , the volume of the steam minus the volume of the water, expressed in calories. The heat absorbed,  $q$ , is the sum of  $\Delta E$ , 498 calories, and  $W$ , 41 calories.

*Example 3—Irreversible Retraction at Constant Temperature with Work Done.* This change of state corresponds more closely than the previous ones to that change of state when rubber is allowed to retract 20 inches (50.8 cm.) a minute in a testing machine. Work is done by the rubber, but as a rule not all of the maximum possible work is done. Since the first law has no limitations concerning whether the work is reversible, the same equations as in Example 2 apply, except that the actual work done is less than the reversible work and as a result less heat would be absorbed, if the change of energy content of the rubber is the same.

*Example 4—Adiabatic Retraction of Stressed Rubber without Doing Work.* If a piece of stretched rubber is allowed to snap to the unstretched condition, no work is done by the rubber, except a negligible amount due to change of volume.

1 gram rubber ( $L = 5 \text{ m.}$ ,  $T_1$ ) = 1 gram rubber ( $L = 1 \text{ cm.}$ ,  $T_2$ )

By Equation 1,  $q = \Delta E + W$

The total increase in energy content is zero, since no heat is absorbed or given out and the work done is zero. It is general experience that the temperature of rubber decreases when allowed to retract without doing work. Within the rubber the energy-content increase due to retraction is counterbalanced by the decrease of energy content due to decreased temperature.

$$0 = dE = \left(\frac{\delta E}{\delta L}\right)_T dL + \left(\frac{\delta E}{\delta T}\right)_L dT \quad (2)$$

$$\left(\frac{dT}{dL}\right) (q = 0, W = 0) = -\frac{\left(\frac{\delta E}{\delta L}\right)_T}{\left(\frac{\delta E}{\delta T}\right)_L} = -\frac{\left(\frac{\delta E}{\delta L}\right)_T}{C_L} \quad (3)$$

In differential form, the change of temperature with the length, if the process is adiabatic and no work is done, is equal to minus the quotient of the change of energy with the length and the specific heat at constant length.

*Example 5—Reversible Adiabatic Retraction of Stressed Rubber.* If stressed rubber retracts adiabatically, performing

its maximum possible work, the energy increase,  $\Delta E$ , is equal to minus the work done, by Equation 1,  $q$  being zero.

$$0 = \Delta E + W \quad (4)$$

In differential form,

$$0 = \left(\frac{\delta E}{\delta L}\right)_T dL + \left(\frac{\delta E}{\delta T}\right)_L dT - f dL \quad (5)$$

$$\left(\frac{dT}{dL}\right)_{(q=0)} = \frac{f - \left(\frac{\delta E}{\delta L}\right)_T}{C_L} \quad (6)$$

The change in temperature with the length when rubber retracts adiabatically and reversibly is equal to the quotient of the force minus the change of energy with respect to length and the specific heat at constant length. In general, a greater decrease of temperature should be observed if rubber retracts adiabatically when work is done than when work is not done.

### Second Law of Thermodynamics

The great value of the second law of thermodynamics lies in its ability to give qualitative expression to the tendency of irreversible processes to take place. A chemical reaction in a test tube, capable of doing work, is irreversible since no work is done. Chemical affinity, or the tendency of a reaction to proceed spontaneously, is the "distance" from equilibrium. The units of the "distance" from equilibrium are entropy units. The second law of thermodynamics states that "in any irreversible process the total entropy of all the systems concerned is increased" (8). Also, in a reversible process the total increase in entropy of all systems is zero. The increase in entropy of a part of a system is counterbalanced by an equal decrease in the remainder. There is only one way to measure change of entropy quantitatively. It is necessary to use a reversible process for the practical reason that it is the only process in which the total change of entropy is known—namely, zero. For a retraction of rubber the rubber itself is part of the system and the thermostat is the other part. The change in entropy attending the reversible retraction of the rubber is counterbalanced by an equal and opposite change in the thermostat. The increase in entropy of either part of the system is numerically equal to the heat absorbed divided by the absolute temperature.

$$dS = q/T \quad (7)$$

Combining with Equation 1,

$$T dS = dE + dW \quad (8)$$

Later, it will be necessary to make use of the fact that entropy, like energy content, depends only upon the state of the substance, and therefore is a perfect differential.

*Example 6—Reversible Retraction at Constant Temperature.* It may seem artificial to imagine rubber to retract and do work as required by an equilibrium stress-strain curve, but such



a procedure is the custom in the application of the second law of thermodynamics. Thus the Carnot cycle for steam gives the theoretical efficiency of a steam engine. The reversible electromotive force of a galvanic cell is used in thermodynamics instead of the electromotive force, which is obtained when a finite current is produced. It is assumed here that the equilibrium stress-strain curve is reversible. If the rubber retracts reversibly, the following analysis is valid for the change of state:

1 gram rubber ( $L + dL$ ,  $T = 25^\circ \text{ C.}$ ) = 1 gram rubber ( $L$ ,  $T = 25^\circ \text{ C.}$ )

By the first law,  $q = dE + dW$  (1)

By the second law,  $q = T dS$  (7)

Combining (1) and (2),  $T dS = dE - f dL$  (8)

Rearranging,  $f = -T \left( \frac{\partial S}{\partial L} \right)_T + \left( \frac{\partial E}{\partial L} \right)_T$  (9)

Differentiating,  $\left( \frac{\partial f}{\partial T} \right)_L = -T \left( \frac{\partial^2 S}{\partial T \partial L} \right) - \left( \frac{\partial S}{\partial L} \right)_T + \left( \frac{\partial^2 E}{\partial T \partial L} \right)$  (10)

For constant length Equation 8 becomes:

$$(dS)_L = \left( \frac{dE}{T} \right)_L \quad (11)$$

Whence,

$$\left( \frac{\partial S}{\partial T} \right)_L = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_L \quad (12)$$

Differentiating,

$$\left( \frac{\partial^2 S}{\partial T \partial L} \right) = \frac{1}{T} \left( \frac{\partial^2 E}{\partial T \partial L} \right) \quad (13)$$

From Equations 10 and 13 it follows:

$$\left( \frac{\partial f}{\partial T} \right)_L = - \left( \frac{\partial S}{\partial L} \right)_T \quad (14)$$

Since the rate of change of entropy with length at constant temperature is negative, it is seen by Equation 14 that at an increased temperature the rubber would be stiffer. It will be noted in Table II that for the load used the rubber is stiffer at the higher temperature. Therefore, the measurements made with the technic of the equilibrium stress-strain curves are capable of giving agreement with the predictions based on the second law and the Joule effect according to Equation 14. In contrast with this result, the usual stress-strain curves do not always give such agreement.

*Example 7—Reversible Adiabatic Retraction of Rubber.* If rubber retracts reversibly and adiabatically, the change of state is accomplished by a process in which the heat absorbed by the rubber,  $q$ , is zero and the entropy remains constant. In this case the heat effects are produced in the rubber instead of in a thermostat.

The following discussion is equivalent to that of Le Blanc and Kröger (7):

1 gram rubber ( $L + dL$ ,  $T + dT$ ) = 1 gram rubber ( $L$ ,  $T$ )

Since the pressure is constant and since entropy is a perfect differential,

$$0 = dS = \left(\frac{\delta S}{\delta T}\right)_L dT + \left(\frac{\delta S}{\delta L}\right)_T dL \quad (15)$$

$$\left(\frac{dT}{\delta L}\right)_S = -\left(\frac{\delta S}{\delta L}\right)_T \div \left(\frac{\delta S}{\delta T}\right)_L \quad (16)$$

$$\left(\frac{dT}{\delta L}\right)_S = -\frac{T}{C_L} \left(\frac{\delta S}{\delta L}\right)_T = -\left(\frac{\delta q}{\delta L}\right)_T \div C_L = \frac{T}{C_L} \left(\frac{\delta f}{\delta T}\right)_L \quad (17)$$

By Equation 17 the adiabatic change of temperature with retraction is equal to the heat absorbed for that retraction at constant temperature divided by the specific heat of the rubber at constant length. Also at low extensions the adiabatic change of temperature is opposite in sign ( $\delta$ ) to that at higher extensions. If this is true, then for smaller extensions the rubber is stiffer at lower temperatures.

*Example 8—The Free Energy.* The free-energy content,  $A$ , is related to maximum reversible work,  $W$ , at constant temperature, by the relation,

$$dA = -dW = fdL \quad (18)$$

1 gram rubber ( $L + dL$ ,  $T = 25^\circ \text{C.}$ ) = 1 gram rubber ( $L$ ,  $T = 25^\circ \text{C.}$ )

$$\left(\frac{\delta A}{\delta L}\right)_T = f \quad (19)$$

Differentiating and using Equation 14,

$$\left(\frac{\delta^2 A}{\delta L \delta T}\right)_L = -\left(\frac{\delta S}{\delta L}\right)_T \quad (20)$$

The free-energy content of stressed rubber is simply related to the force and the strain. The temperature coefficient is also simply related to the entropy of the rubber.

#### Very Rapid Stress-Strain Curves

Williams (16) has obtained very rapid stress-strain curves for 250 per cent elongation which show no hysteresis. He has stated that "the curves were carried to only a relatively low elongation in order that the load imposed would not be great enough to cause plastic flow." Moreover, equilibrium stress-strain curves which exhibited no hysteresis have been obtained by the writer for elongations as high as 600 per cent.

Williams has attributed the absence of hysteresis in very rapid stress-strain curves to the absence of plastic flow in the rubber, because of the shortness of the time interval. It would be difficult, but not by any means impossible, to apply the laws of thermodynamics, and especially the concepts of energy or entropy content, to the stressed rubber at any instant of its brief stress-strain curve history. The second law of thermodynamics requires that changes of state be brought about by reversible processes; it does not require that an equilibrium should be the more stable one. For example, the equilibrium between supercooled liquid water and water vapor, at a temperature below the freezing point, is less stable than the equilibrium between ice and water. Both equilibria are reversible and the energy or entropy content of the supercooled liquid water has a real significance. Likewise the

instantaneous equilibrium between the rapidly stretched rubber and the force at any instant can be real, even though unstable with respect to the equilibrium between stretched rubber and a force applied by a given load, which has been oscillated. The difference between the transient state of rubber in the rapid stress-strain curve and the steady state of the rubber in the equilibrium stress-strain curve may be stated as follows: The rubber in the transient state has not exhibited plastic flow, whereas the rubber in the steady state has exhibited plastic flow. If very rapid stress-strain curves are reversible, the application of the second law of thermodynamics to rapidly stretched rubber is limited to states of the rubber whose existence is very transient.

### Discussion

The usual stress-strain curves which are run at 20 inches (50.8 cm.) per minute show vulcanized rubber to be less stiff at higher temperatures. This is disconcerting, since the Joule heat effect on extension or retraction, together with the second law of thermodynamics, demands that vulcanized rubber should be stiffer at higher temperatures if it behaves reversibly. However, the customary stress-strain curves show hysteresis, and this is direct evidence of irreversibility. Mechanical reversibility requires that the same point on the stress-strain curve shall be obtained whether it is observed by approaching equilibrium from higher or lower strain or from higher or lower temperature.

By oscillating a strip of rubber, loaded with a weight, in the neighborhood of its equilibrium length, it is found that the equilibrium length is independent of the direction from which equilibrium is approached. The rubber could be initially either in the stretched or retracted state. Such a stress-strain curve, therefore, exhibits reversibility and also shows the rubber to be stiffer at higher temperature in accord with the Joule heat effect and the second law of thermodynamics. The essential difference between the customary and the equilibrium stress-strain curve is that time or frictional effects enter when the rubber is stretched at a given velocity. In the equilibrium stress-strain curve these effects are eliminated.

The absorption of shocks and vibrations by rubber in a practical sense depends upon the fact that the stress-strain curve shows hysteresis under these conditions. Thus, oscillations in the rubber are damped. Consequently the second law of thermodynamics cannot be applied to such irreversible actions.

The potential energy of stretched rubber is the tendency to do work and increases with the stretch. On the other hand, the energy content, as defined by the first law of thermodynamics, decreases with the stretch, for when rubber retracts without doing work the temperature decreases. This is all the more interesting since up to 600 per cent elongation the equilibrium stress-strain curves are identical for different

cures, in contrast with the usual stress-strain curves which show the rubber to be stiffer with higher cures. This is additional evidence that vulcanization does not greatly affect the elastic properties. The important change in rubber caused by vulcanization is a greater resistance to the plastic flow or permanent set.

#### Acknowledgment

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## Rate of Cure of Reclaimed Rubber—II<sup>1</sup>

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The work recorded in this paper supplements previously recorded experiments showing that the alkali content of reclaim is only partially responsible for its rapid rate of cure. Extraction of alkali-cooked reclaim with water for 60 days extracted three times as much alkali as was found by the ordinary alkalinity control test (4 hours). Adding this quantity of alkali in glycerol as a carrier to water-cooked reclaim brought the rate of cure up to that of the alkali-cooked reclaim. The new data confirm the negative effect of combined sulfur on the rate of cure of reclaim. Other data indicate that residual accelerator (di-*o*-tolylguanidine) and oxidation products in the reclaim do not affect the rate of cure. Residual alkali is largely the cause of the rapid rate of cure of reclaim.

**T**HAT the rapid rate of cure of rubber stocks containing reclaimed rubber is due only in part to the alkali used in the reclaiming process and that some other factor is also responsible has been shown by experiments previously reported (3). In continuing the investigation the five logically possible causes of the rapid rate of cure which were listed by Shepard, Palmer, and Miller, the first investigators, were considered. These are: (1) residual alkali in the reclaim; (2) unchanged accelerator in the reclaim; (3) depolymerization by the action of heat and mastication; (4) "head start" of the reclaim with respect to chemical state of cure; (5) oxidation products acting as curing agents. The first, third, and fourth possible causes only were considered in the previous report. All of them are covered briefly in this paper, with special emphasis on residual alkali.

Martin (1) has pointed out that small amounts of alkali

<sup>1</sup> Received October 7, 1929.

accelerate and large amounts of either acid or alkali retard the vulcanization of rubber. Twiss (4) has reason for believing that in using caustic as an accelerator of vulcanization a carrier medium of such a nature that it disperses in the rubber on the mill must be used. Such a medium, glycerol for example, facilitates dispersion of the caustic in the rubber.

### Methods and Apparatus

A small steel autoclave (3) was used as an experimental devulcanizer. Commercial "hogged" scrap and "synthetic" scrap made in the laboratory were used for reclaiming. Reclaimed scrap from the devulcanizer was washed in four or five changes of water, dried at 60–70° C. overnight, and refined by passing between tight rolls (0.025 cm. apart). In tire reclaim produced by a water cook, the cords were removed by washing the reclaim on a laboratory washing mill.

In compounding rubber stocks containing reclaim, care was taken to obtain rubber from the same sheet, in some cases massing it, for use in any one series of stocks. The milling of each series was completed in one day. The same was true of the curing and of the testing. The rate of cure was judged by using the optimum modulus as an index, as this property is less affected by experimental errors in testing than any other. All compounds discussed in this paper are reported on the basis of 100 parts of rubber, this always including the rubber in the reclaim.

### Effect of Alkali

In the previous work on the effect of alkali (3), caustic was added to rubber in aqueous solution (2.4 N). Because of the desirability of such a carrier as glycerol in dispersing caustic soda, as pointed out by Twiss (4), a glycerol-sodium hydroxide mixture was used. A cellulose-sodium hydroxide paste, obtained by concentrating the spent liquor from a caustic cook, was used in one case. (By cellulose, cellulose decomposition products are to be understood.)

A water-cooked reclaim made from whole tire scrap from two devulcanizer runs, 6 hours at 174–190° C., was prepared for comparison with an 8 per cent caustic-cook reclaim (8 hours at 193° C.) from the same scrap. The alkalinity of these two reclaims was determined by boiling a 50-gram sample for several hours with distilled water, rinsing the sample, and reheating overnight on a steam plate. The alkali so extracted was titrated with 0.1 N sulfuric acid, using methyl red as the indicator. It amounted to 0.15 per cent (calculated as sodium hydroxide) for the alkali reclaim and 0.02 per cent for the water-cook reclaim. A further overnight treatment resulted in an additional 0.02 and 0.002 per cent of alkali. The percentages 0.17 and 0.02 were thought to represent practically all the alkali present. On this basis the reclaims were compounded with new rubber as shown in Table I.



The glycerol-sodium hydroxide solution contained 21.2 per cent of sodium hydroxide and the cellulose-sodium hydroxide solution contained 8.7 per cent.

The data as represented in Figure 1 show that the caustic-cooked reclaim compound (1) containing 0.06 per cent of sodium hydroxide reached its optimum cure in 20 minutes, while the water-cooked reclaim compound (2) and the compounds containing 0.06 (3), 0.15 (4), and 0.15 (5) (cellulose-sodium hydroxide paste) per cent of added alkali were somewhat slower in reaching their optimum cures. However, the rates of cure of the stocks containing water-cooked reclaim plus added alkali are in line with the amount of alkali added, and the compound containing 0.30 per cent sodium hydroxide (6) has a rate of cure approximately as fast as the alkali-reclaim control stock (1). It was concluded that the alkalinity analysis upon which the compounding of compound 3 was based (0.06 per cent sodium hydroxide) might have been incomplete and a more complete extraction was therefore attempted.

Reclaim from two alkali cooks similar to the foregoing was blended to make one sample. Reclaim from two water cooks was similarly blended. Then 50-gram samples of these were sheeted out and extracted in 800 cc. of boiling water during the daytime and in the same amount of water at approximately 70° C. at night. Some 60 extractions were made, the water at first being changed every 4-6 hours during the day. Later the water was changed daily and toward the end of the extraction only every 2 or 3 days. The extracts were titrated at room temperature with 0.1 N sulfuric acid, using methyl red and phenolphthalein as indicators. Blank titrations were conducted under identical conditions. When the alkalinity titrations for each successive period were no larger than those of the blanks the determination was considered complete.

The water-cooked reclaim contained no material alkaline to phenolphthalein and after 11 extractions the sample had given up its entire alkali content. After 27 titrations the caustic-reclaim extract failed to show phenolphthalein alkalinity. Sixty extractions were required to remove all of the material alkaline to methyl red. After correcting for the blank titrations the results shown in Table II were obtained.

The results in Table II indicate the presence in the alkali

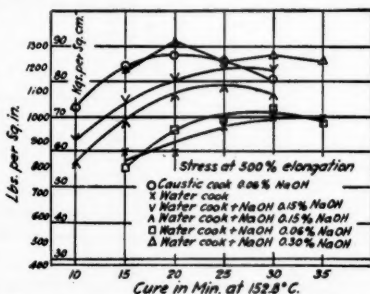


Figure 1—Effect of Added Alkali on Rate of Cure of Water-Cooked Reclaim

Table I

COMPOUND	SMOKED SHEETS	ALKALI RECLAIM	WATER-COOKED RECLAIM	ZINC OXIDE	SULFUR	DI-O-TOLYL- GUANIDINE	GLYCEROL- NaOH	CELLULOSE NaOH	TOTAL	NaOH R %	NaOH Compd. %
1	68.4	51.2		6.8	2.7	0.7	..	...	139.8	0.08	0.06
2	68.4	..	51.2	6.8	2.7	0.7	..	...	139.8	0.00	0.00
3	68.4	..	51.2	6.8	2.7	0.7	0.36	...	130.16	0.08	0.06
4	68.4	..	51.2	6.8	2.7	0.7	0.9	...	130.7	0.19	0.15
5	68.4	..	51.2	6.8	2.7	0.7	1.86	2.2	132.0	0.19	0.15
6	68.4	..	51.2	6.8	2.7	0.7	1.86	...	131.66	0.39	0.30

cook of both free sodium hydroxide and sodium salts of weak acids. As these weak acids were not identified, the results were calculated as sodium hydroxide. In adding sodium hydroxide to water-cooked reclaim stocks, undoubtedly some of the alkali forms such salts while some remains as free alkali. Both probably act as accelerators.

The standard method of determining alkalinity for factory control work consists in boiling in water a thinly sheeted 25-gram sample for 4 hours, replacing the water which boils off. The extract is then squeezed from the sample, which is rinsed with hot distilled water. This washing is repeated 7 or 8 times and the combined rinsings and extract are titrated with 0.1 *N* acid, using methyl red as indicator. This method indicated that the sample of alkali-cooked reclaim contained 0.45 per cent of alkali calculated as sodium hydroxide. Obviously this shorter method of analysis was incomplete, as had already

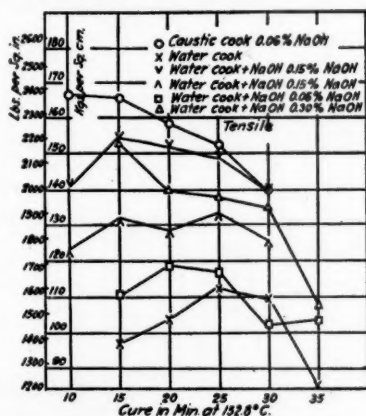


Figure 2—Effect of Added Alkali on Rate of Cure of Water-Cooked Reclaim Stock

been shown (3). The two reclaims were compounded as shown in Table III, the letters in parenthesis referring to Figure 3.

RECLAIM STOCK	END POINT WITH	
	Phenolphthalein	Methyl Red
	% NaOH	% NaOH
Alkali-cooked	0.27	1.46
Water-cooked	..	0.017

The glycerol-sodium hydroxide compound contained 15.8 per cent sodium hydroxide. Compound 10 was a water-cooked reclaim from the same scrap but was not analyzed. Compounds 7 and 11 would have identical alkali content if the phenolphthalein alkalinity only of the alkali reclaim were to be considered. Compound 8 was run twice, as the results, represented by *x* in Figure 2, were based on somewhat erratic data, which, however, are exactly represented in the figure.

Table III

COMPOUND	SMOKED SHEETS	ALKALI RECLAIM	WATER- COOERD RECLAIM	ZINC OXIDE	SULFUR	DI-O-TOLYL- GUA- NIDINE	GLYCEROL- NAOH	TOTAL	NAOH R %	NAOH COMPD. %
7 (a)	68.4	51.2	51.2	6.8	2.7	0.7	...	129.8	0.75	0.58
8 (b and f)	68.4	..	51.2	6.8	2.7	0.7	4.7	134.5	0.75	0.58
9 (c)	68.4	..	51.2	6.8	2.7	0.7	...	129.8	0.00	0.00
10 (d)	68.4	..	51.2	6.8	2.7	0.7	0.9	130.7	0.00	0.11
11 (e)	68.4	..	51.2	6.8	2.7	0.7	...	129.8	0.14	0.00
12 (g)	68.4	51.2 <sup>a</sup>	..	6.8	2.7	0.7	...	129.8	0.00	0.00

<sup>a</sup> Extracted.

Sufficient glycerol was added to equalize the glycerol content of all the stocks.

Figure 3 shows that the amount of alkali found by analysis in the alkali-cooked reclaim (using the methyl red figure) when added to a stock containing water-cooked reclaim produced a rate of cure equivalent to that of the stock containing alkali-cooked reclaim. A smaller amount of alkali, based on the phenolphthalein end point of the titration, was insufficient to reproduce the rate of cure of the control stock. Data on compound 12 (g) were meager, owing to scarcity of extracted reclaim, but the indications are that the extraction slowed up the rate of cure to approximately that of the stocks containing water-cooked reclaim alone.

To compare the rate of cure of water-cooked and alkali-cooked reclaim with new rubber, a pure gum stock (13) was cured for 2 hours at 143.3° C. and used for scrap. This compound is given in Table IV.

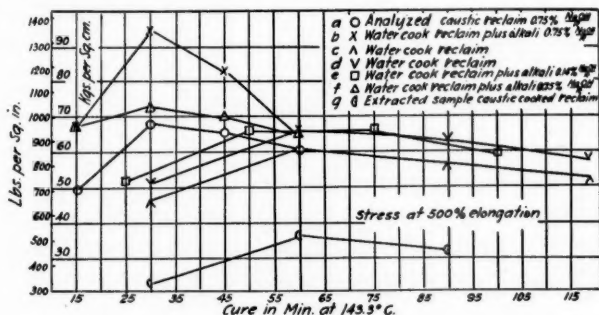


Figure 3—Comparison of Water-Cooked and Caustic-Cooked Reclaim with Alkalinity Compensated

The scrap was devulcanized by two methods, one by heating in water for 5 hours at 185° C. and the other by heating in 8 per cent caustic for 5 hours at 190° C. To ascertain the effect of acid neutralization of residual alkali, a portion of each of these reclaimed scraps was heated for 24 hours in a 25 per

Table IV

COM- POUND	SMOKED SHEETS	PALE CREPE	SULFUR	ZINC OXIDE	RE- CLAIM	DI-O- TOLYL- GUANIDINE	TOTAL
13	100.0	...	5.4	2.7	...	...	108.1
14	69.5	...	2.6	3.3	32.6	0.7	108.7
15	...	100.0	...	2.7	...	...	102.7
16	...	69.5	2.6	3.3	32.6	0.7	108.7

cent hydrochloric acid solution at approximately 70° C. All four products were thoroughly washed on a laboratory washing mill, dried, and refined. The results of the sulfur analyses are given in Table V.

These reclaims were compared in a compound (14) containing 30 per cent reclaim. Adjustments were made for the free sulfur content of the reclaim. The data (Figure 4) show that

in spite of thorough washing the alkali reclaim was distinctly faster than the water-cooked product. The acid-treated reclaims were slower than the controls, though the exact location of the optimum cure was not ascertained. As both water-cooked and alkali-cooked reclaim stocks were retarded by the acid treatment, it is probable that residual acid was the cause.

Table V

TREATMENT	TOTAL SULFUR <sup>a</sup>	FREE SULFUR <sup>a</sup>
	Per cent	Per cent
Water cooked	5.92	0.21
Water cooked, acid washed	5.77	0.13
Alkali cooked	3.03	0.09
Alkali cooked, acid washed	2.72	0.20

<sup>a</sup> Based on rubber.

In comparing new rubber with water-cooked reclaim, a compound containing no sulfur (15) was mixed, using pale crepe rubber. The sulfur was left out, so that the stock would not cure when heated.

Compound 13 was re-mixed, using pale crepe instead of smoked sheets, and was cured 2 hours at 143.3° C. This scrap and a portion of the uncured rubber mix were heated in separate compartments of the autoclave for 2.5 hours at 186° C. in water.

For the purpose of comparing these two products with unheated rubber, com-

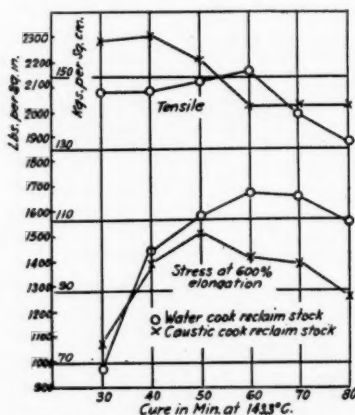


Figure 4—Comparison of Water-Cooked and Caustic-Cooked Reclaims of Rubber—S-ZnO Stock for Rate of Cure

compound 16 was used, the uncured new rubber compounds 15 (heated and unheated) being substituted in No. 16 to the extent of 32.6 parts just as if they were reclaims. The data obtained are shown in Figure 5.

The cure of new rubber was slower than that of water-cooked reclaim. To what cause this may be due has not been determined. Incidentally, in the previous report on these studies (3) several comparisons show new rubber and water-cooked reclaim to have identical rates of cure, while in one case the reclaim was faster than new rubber. The results in Figure 5 confirm previous conclusions (2) that the rate of cure of rubber is not affected by heat, when disubstituted guanidines are used as accelerators.

#### Effect of Combined Sulfur

Previous study had indicated that in three out of four experiments the rates of cure of water-cooked reclaim and of



new rubber control were identical, irrespective of combined sulfur content. In the fourth case a high-sulfur (2.5 per cent) reclaim stock was somewhat faster than a low-sulfur (1.4 per cent) reclaim stock or the new rubber control. Data on another pair of high (3.7 per cent) and low (1.3 per cent) reclaim stocks are shown in Figure 6. These reclaims were prepared from the compounds in Table VI.

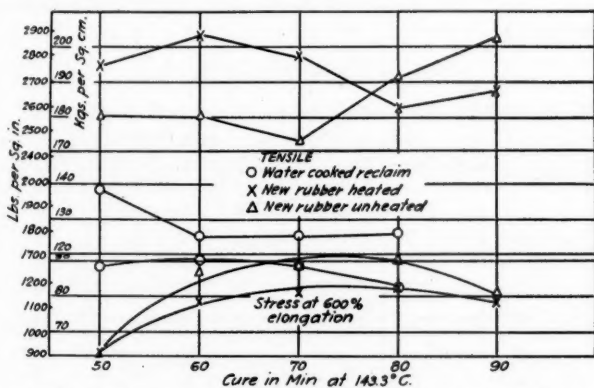


Figure 5—Comparison of Water-Cooked Reclaim vs. New Rubber for Rate of Cure

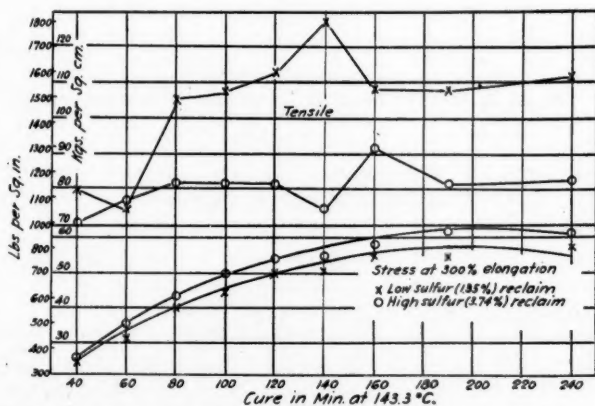


Figure 6—Effect of Variation in Combined Sulfur on Rate of Cure of Reclaim in a Tread Stock

Table VI

COM- POUND	SMOKED SHEETS	ZINC OXIDE	SULFUR	TETRAMETHYL- THURAM DISULFIDE	TOTAL
17	100	4	5	0.3	109.3
18	100	4	1.5	0.3	105.8

These stocks were cured for 45 minutes at 132° C. and devulcanized for 8 hours at 185° C. in water.

These reclaims were compounded as shown in Table VII.

Table VII

COM- FOUND	SMOKED SHEETS	RECLAIM		ZINC OXIDE	CARBON BLACK	PINE TAR	SUL- FUR	TOTAL
		High (3.7)	Low (1.3)					
19	51.7	51.7	..	25.8	34.5	5.2	3.5	172.4
20	51.7	..	51.7	25.8	34.5	5.2	3.5	172.4

The data (Figure 6) show that within experimental error no difference in the rate of cure is caused by this difference in combined sulfur (2.4 per cent). The low sulfur reclaim has a higher tensile, due no doubt to its lower sulfur content and consequently increased plasticity.

#### Effect of Residual Accelerator

To determine the possible effect of residual accelerator or accelerator decomposition products, a tread stock with and without the accelerator di-o-tolylguanidine was reclaimed for

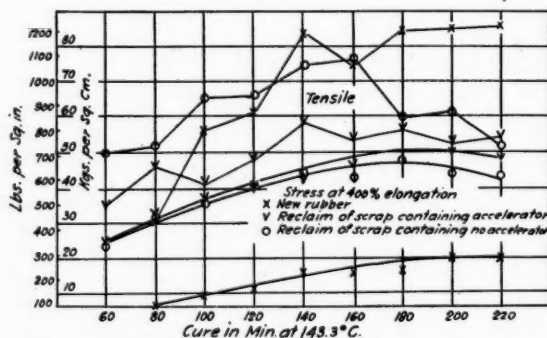


Figure 7—Effect of Residual Accelerator on Rate of Cure of Reclaim

15 hours at 185° C. in water. Pine tar (2 per cent) was added to the scrap as a plasticizing agent. The formulas are given in Table VIII.

Table VIII

COM- FOUND	SMOKED SHEETS	ZINC OXIDE	CARBON BLACK	PINE TAR	SULFUR	DI-O- TOLYL GUA- NIDINE	TOTAL
21	100	34	32	5.3	6.3	0.9	178.5
22	100	34	32	5.3	6.3	...	177.6

Compound 21 was cured for 25 minutes at 147° C. and compound 22 for 100 minutes at 147° C.

These stocks with their cures gave comparable states of cure. After the reclaiming, compounds 23, 24, and 25, a control with pigments compensated, were mixed as shown in Table IX.

Table IX

COM- FOUND	SMOKED SHEETS	RECLAIM		ZINC OXIDE	CARBON BLACK	PINE TAR	SUL- FUR	TOTAL
		Ac- cel- erated	Unac- cel- erated					
23	64	64	..	8.1	..	..	3.1	139.2
24	64	..	64	8.1	..	..	3.1	139.2
25	100	..	..	21	11.6	3.2	3.1	138.9

The rates of cure of the stocks containing reclaim of accelerated and unaccelerated scraps were not appreciably different (Figure 7), nor was the rate of the new rubber control far from that of the stocks containing reclaim.

### Effect of Oxidation

The comparison here given is not exact, as the reclaims, prepared in the presence of oxygen and in its absence, were made with caustic. Data already presented show that small differences in caustic content can appreciably affect the rate of cure. The results are presented, however, to show that oxidation cannot be highly effective in increasing the rate of cure.

Whole tire reclaim was devulcanized in the autoclave, in one case in the presence of oxygen and in the second case with the air removed. The second reclaim was dried under reduced pressure in nitrogen, while the control was dried in air as usual. Both reclaims received the customary washing

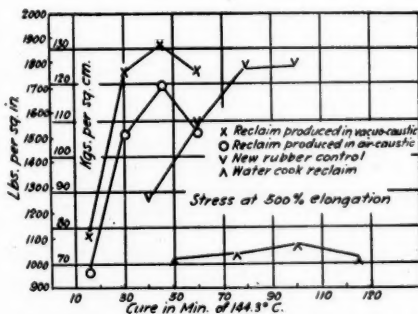


Figure 8—Effect of Reclaiming in Inert Atmosphere on Rate of Cure of Reclaim

and refining. The compounding of these reclaims was done in the test formula 1 containing 40 per cent reclaim. The data obtained, with those on a new rubber control and a stock containing water-cooked reclaim introduced for comparison only, are presented in Figure 8. No difference in rate of cure is observable between the stocks containing, on the one hand, oxidized reclaim, and, on the other, reclaim protected from oxidation. As identical washing procedures were followed in making these reclaims, it is probable that the difference in their alkali contents, which if large would invalidate this comparison, is small. It may be concluded therefore that oxidation is not a factor in the rapid rate of cure of reclaim.

### Water-Cooked Reclaim with Added Alkali

Table XI and Figure 9 show the effect of adding sodium hydroxide in glycerol to a stock containing water-cooked

reclaim. The glycerol content was made the same for all five stocks. The accelerator (NaOH) content was varied as shown in Table X.

Table X

COM- POUND	SMOKED SHEETS	WATER- COOKED RE- CLAIM	ZINC OXIDE	GLYC- EROL	GLYC- EROL- NaOH	SUL- FUR	DI-O- TOLYL- GUAN- IDINE	TOTAL	NaOH R %
26	85.0	26.3	6.9	11.3	...	2.8	0.7	133.0	0.0
27	85.0	26.3	6.9	10.5	0.8	2.8	0.7	133.0	0.12
28	85.0	26.3	6.9	7.5	3.8	2.8	0.7	133.0	0.59
29	85.0	26.3	6.9	3.8	7.5	2.8	0.7	133.0	1.19
30	85.0	26.3	6.9	..	11.3	2.8	0.7	133.0	1.77

The data in Table X indicate that with increase in alkali content there are produced (1) increased rate of cure, (2) higher modulus and tensile, and (3) improved aging qualities. The presence of 0.6 per cent sodium hydroxide on the rubber approximately doubles the rate of cure, raises the modulus and

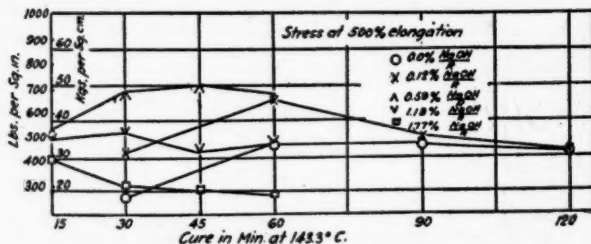


Figure 9—Effect of Added Alkali on Rate of Cure of a 20 Per Cent Water-Cooked Reclaim Stock

tensile 50 per cent, and improves aging approximately 20 per cent. The aging period is, of course, unnecessarily long.

Table XI

COM- POUND	NaOH R %	CURE AT 143.3° C. Min.	NORMAL TESTS		AGED 21 DAYS AT 70° C.		DE- PRECI- ATION IN TENSILE %	AVER- AGE %
			Stress at 500% E.	Tensile at break	Stress at 200% E.	Tensile at break		
			Kg./ cm. <sup>2</sup>	Kg./ cm. <sup>2</sup>	Kg./ cm. <sup>2</sup>	Kg./ cm. <sup>2</sup>		
26	0.0	30	19	99	4.4	14.5	85.3	87.5
		60	33	131	8.0	13.7	89.5	
		90	33	115	8.8	14.1	87.7	
		120	31	109				
27	0.12	30	31	140	7.7	42	70.0	81.4
		60	46	151	11.0	23	84.8	
		90	36	134	10.3	14.2	89.4	
		120	32	128				
28	0.59	15	38	170	8.4	77	54.7	70.8
		30	49	197	11.2	44	77.6	
		45	50	180	11.8	36	80.0	
		60	47	192				
29	1.19	15	35	186	7.4	55	70.4	
		30	37	167	9.3	70	58.1	
		45	31	183	9.7	25	84.6	
		60	33	140	7.5	22	84.3	
30	1.77	15	29	156	5.7	42	73.0	
		30	22	142				

### Summary and Conclusions

Residual alkali in reclaim is chiefly responsible for the faster rate of cure of stocks containing reclaimed rubber as

compared with those containing new rubber only. Reclaim prepared in water can be made to cure as fast as alkali reclaim by the addition of sodium hydroxide to the extent that this is present in the alkali reclaim.

The determination of residual alkali requires a very long extraction, in this case approximately 60 days.

Of five possible theories accounting for the rapid rate of cure of reclaim, only that of residual alkali is tenable. There still remains in certain cases, however, a difference in rate of cure between stocks containing new rubber and those containing water-cooked reclaim for which no explanation has been found.

Sodium hydroxide of itself is not deleterious to rubber compounds, for, in addition to its value as an accelerator in certain cases, it tends to improve physical properties and aging resistance, as judged by the Geer oven test.

#### Acknowledgment

The writers wish to make acknowledgment to N. A. Shepard for direction in this work and for helpful criticism in the writing of this paper.

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## Estimation of the Degree of Penetration of Rubber into Fabrics<sup>1</sup>

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**I**T IS frequently important to know to what extent fabrics are impregnated with rubber in the course of manufacture of various fabric-rubber combinations, such as tires, belts, footwear, etc. Such information is of value in answering questions relative to fabric fatigue in service, adhesion, resistance to corrosion, and others.

Direct microscopic examination of thin sections of fabric-rubber structures presents mechanical and optical difficulties, chief of which is the practical impossibility of cutting perfect sections. The lack of optical contrast between textile fibers and many rubber compounds is another objection to this method which differential staining has not successfully overcome. Etching the surfaces of thick sections and examination by reflected light are only partially successful in securing the requisite detail.

The method described has been used in this company's laboratories for several years with considerable success. It is simple, relatively rapid, demands no equipment beyond that found in the average laboratory, and requires no unusual degree of skill.

The rubber in the sample to be investigated is cured to the hard-rubber stage to prepare it for sectioning. There are some references in the literature to methods of hardening soft rubber in order to make sectioning easier. They recommend the use of molten sulfur, sulfur chloride, or liquid air, but these materials have not been found satisfactory for use in the preparation of fabric-rubber sections.

<sup>1</sup> Received October 7, 1929. Presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, N. J., September 26 to 28, 1929.





A. No cure



B. 90 minutes at 292° F., no pressure



C. 90 minutes at 292° F., 50 lbs./sq. in.



D. 90 minutes at 292° F., 150 lbs./sq. in.



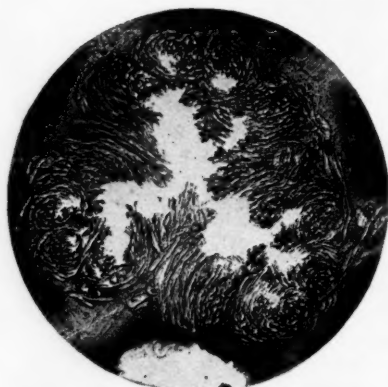
E. 90 minutes at 292° F., 300 lbs./sq. in.



F. 90 minutes at 292° F., 500 lbs./sq. in.

Figure 1.—Tire Cords, 23 s/5/3 Double-Coated with High-Gum Compound and Cured 90 Minutes at 144° C. (292° F.) in a Plunger Mold

Usually, samples about 1 cm. (0.5 inch) wide and 5 cm. (2 inches) long are adequate. If these are not rubber-coated on both sides, it is well to cover the exposed fabric with thin strips of uncured stock to lend support in cutting the sections. The samples are submerged in aqueous solutions of polysulfides (saturated solutions of sodium or calcium polysulfides have given the best results) containing an excess of sulfur on the rubber. Water-soluble accelerators, such as hexamethylenetetramine, may be added, up to 20



A. Double-coated high gum compound



B. Double-coated high reclaim compound



C. Latex dipped



D. Cement dipped

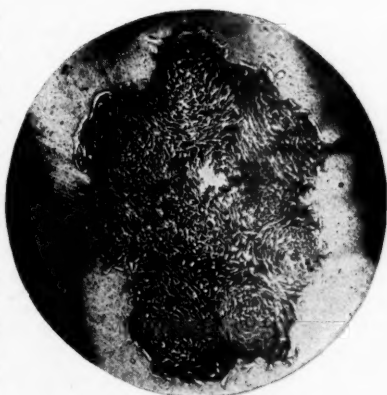
Figure 2—Tire Cords 23's/5/3 from Finished Tires

per cent on the sulfur, to improve the cure. The cured hard rubber should be horny and flexible, not brittle. Most compounds reach this stage at cures of 12 to 15 hours. A good average cure is: 30 minutes' rise to 115.5° C. (240° F.); 2 hours at 115.5° C. (240° F.), open steam; 30 minutes' rise to 149° C. (300° F.); 15 hours at 149° C. (300° F.), open steam. This is most conveniently accomplished by allowing the final part of the cure to take place overnight in a small steam vulcanizer. After washing for a few minutes in clean water and

A. Cheesecloth impregnated with latex by the anode process. (Electrodeposition)



B. Breaker fabric dipped in rubber dispersion



C. Breaker fabric dipped in latex



Figure 3—Miscellaneous Fabrics

drying on a steam bath the specimens are ready for sectioning.

For cutting the sections a simple hand microtome and section razor serve every required purpose. The sections need not be excessively thin; a thickness of 0.050 to 0.100 mm. permits easy handling and sufficient detail in microscopic examination. The cut sections are dropped into concentrated sulfuric acid and allowed to remain until all the cotton fibers have disappeared, after which they are washed in clean concentrated sulfuric acid, mounted under cover glasses on slides in a drop of the same medium, and photographed. It has been impossible, thus far, to find a better mounting medium than this. Clearing the acid from the sections in water, alcohol, or other liquids has the effect of shriveling the fine tendrils of rubber which extend into the interior of the fabric, thus causing loss of detail. The same effect results on days of high humidity when the sulfuric acid absorbs a great deal of moisture. However, sections from a large number of samples may be prepared at one time and stored in separate dishes for a number of hours without serious deterioration. Immediately before photographing they may be immersed for a few minutes in fresh acid to restore them to the proper condition. A linear magnification of 35 to 50 is suitable for most photomicrographs.

Examples of sections showing variations in the degree of impregnation of several kinds of fabric with different treatments are included in the accompanying reproductions.

## Flexing Test for Tire Carcass Stocks<sup>1</sup>

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**T**HE test about to be described has been in use in this company for about fifteen years, and has been adopted to some extent by the rubber industry, particularly for use with belting. However, in response to various requests for information regarding the details of the test as applied to tire-carcass materials, a brief description of the methods now in use in the company laboratories is given here.

The tests consists of taking a strip composed of several plies of fabric and rubber, bending the strip around a hub until its two faces are nearly parallel, applying a weight to the hub so that the strip is pulled taut, and moving the jaws reciprocally so that the strip drives the hub and is moved back and forth around the hub. This is continued until a separation occurs between the plies of the strip.

This test, if carried out under carefully controlled conditions, gives consistent results, and it is the purpose of this paper to outline these conditions.

### Preparation of Flexing Pads

The fabric is calendered under conditions as nearly as possible standard. One of the fundamentals of the test is that, to be comparable, samples must contain equal volumes of rubber. In order to secure this condition, the fabric is gaged carefully before and after calendering, and during the coating operation the rubber itself is gaged.

The construction of the pad itself varies with the type of fabric.

*Square Woven Fabric.* The fabric is frictioned on both sides and skim-coated on one side with a layer 0.051 cm. (0.020 inch) thick. The fabric is cut into pieces 14.0 × 21.6

<sup>1</sup> Received October 7, 1929. Presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, N. J., September 26 to 28, 1929.

cm. ( $5.5 \times 8.5$  inches). Three of these pieces are cut so that the long edge runs with the fabric, and the other two so that the long edge is across the fabric. The pieces are then assembled by a hand roller, in such a way that the skim-coated side of the bottom piece is against the friction of the next, and so on. The first, third, and fifth plies are those in which the long dimension runs with the fabric.

*Cord Fabric and Web Fabric.* Six plies are used in this case. The first, third, and fifth are cut so that the long dimension runs with the fabric, and the second, fourth, and sixth so that the long dimension runs across the fabric. The pad is then assembled with a hand roller, care being taken that the plies are assembled in such a way that the same calendered side on each piece is up.

The pads are now cut by means of a templet and knife to a size of  $12.5 \times 20.2$  cm. ( $4.94 \times 7.94$  inches), using a knife with a thin blade. Care must be taken to have the long edge of the templet as nearly as possible parallel with the longer cords of the pad.

The pads are now gaged and weighed to the nearest gram.

### Curing

In order to obtain uniform results it is necessary to cure the pad in such a way that the cords remain straight, and the plies evenly compressed. To do this care must be used to secure just the right amount of compression of the sample. There are probably a number of ways of doing this, but the one that has been found most satisfactory is as follows:

A mold with a cavity  $12.7 \times 20.3 \times 1.27$  cm. ( $5 \times 8 \times 0.5$  inches) is used. If the fabric has been calendered to make a total thickness of 0.127 cm. (0.050 inch), which is usually the case, the six-ply pad will have a total gage of around 0.762 cm. (0.300 inch). Therefore, it is necessary to make up the difference by adding layers of other material cut to the size of the mold. The materials used are holland cloth, tin-foil, and a pad made of two or three plies of skim-coated fabric which has already been cured and which is of fairly uniform thickness. These materials may be used repeatedly as long as they remain in good condition.

A piece of holland cloth is placed on either side of the pad, a piece of tin-foil is placed over each piece of holland cloth, and the top of the pad—that is, the face in which the cords run across—is covered with a three-ply filling pad. The remainder of the thickness is made up by placing on top of the pad extra holland-cloth or tin-foil fillers, the thickness being measured by putting the pile of fillers and pad in a Randall and Stickney gage and applying a little pressure with the fingers on both sides of the foot. The total thickness should be 1.27 cm. (0.5 inch), the depth of the mold. Expansion will then give just the right pressure to make a compact, yet undistorted, pad.

The flexing pad and filler are then put in the mold, care



being taken to keep uppermost that side of the pad bearing the cross threads. An enclosed press (autoclave press), in which the mold is heated by a completely surrounding atmosphere of steam under pressure, is normally used. In this case a sheet of uncured rubber stock containing curing ingredients, about 0.05 cm. (0.02 inch) thick, and measuring  $15.2 \times 22.9$  cm. ( $6 \times 9$  inches), is put over the cavity before the cover of the mold is placed in position. This covers the overflow space and effectually seals the mold. If such a sheet is used, its thickness is included in the determination of the total thickness of the pad and fillers. The holland and tin-foil sheets on the under side of the pad permit it to be readily removed from the mold.

Pads made and cured in this manner measure  $12.7 \times 20.3$

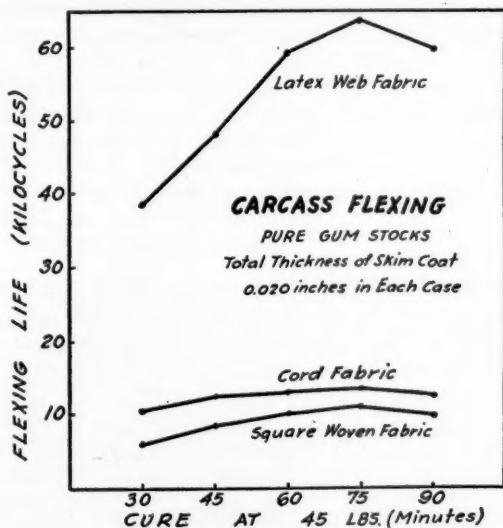


Figure 1—Flexing Life with All-Rubber Friction and Skim Coats

cm. ( $5 \times 8$  inches) and when cool the six-ply pads have a thickness of 0.698 to 0.711 cm. (0.275 to 0.280 inch). The thickness should be quite uniform over the area of the pad except at the upper edges, where there should be slight signs of overflow. A record is kept of the weight and gage of the pad.

When five-ply pads made of square woven fabric are used, two pads may be cured in the same mold with the skim-coat surfaces facing each other.

In earlier work an attempt was made to duplicate more nearly the conditions existing in curing core-built tires in a mold by curing thick layers of tread stock on top of the carcass stock. This method was abandoned because it caused distortion.

Although the curing conditions described are rigidly fol-

lowed, it is quite likely that with pads of other thicknesses more or less compression might be found desirable. The important thing is to find a set of calendering and curing conditions which gives a dense yet undistorted pad, to standardize on this, and to deviate as little as possible from these conditions.

### Preparation of Strips

The flexing pad should stand not less than  $1\frac{1}{2}$  or 2 days between curing and testing. The pads are cut into four strips each 2.54 cm. (1 inch) wide and 20.3 cm. (8 inches) long. On the first cut about 0.6 to 1.3 cm. (0.25 to 0.5 inch) of selvage along the long side is discarded. Care must be taken to cut the strips straight and as closely to exact width as possible. If reasonable care has been taken in preparing the pads, there should not be more than five or six cut threads showing on the two cut sides of a six-ply strip. The term "cut threads" as used here refers only to those running lengthwise of the strip, and not to those running crosswise. An excessive number of cut threads indicates that many of the threads of alternate plies are not parallel. It is desirable to have as many as possible of the long threads held by the jaws. Where there is a large number of cut threads, the heavy weight of the flexing machine is held by fewer threads, which tends to permit greater stretching.

The test samples are run with the long threads touching the hub of the flexing machine in the case of cord and web fabric. In the case of square woven fabric the friction side touches the hub. The hub has a diameter of 1.43 cm. (0.56 inch) for tire carcass work. The weight suspended from each sample is 45.36 kg. (100 pounds). Only in special cases is this weight changed. Care must be taken that the load is exactly 100 pounds, and this should be checked occasionally by the dead-weight method. The flexing results are not proportional to the load.

A thick coat of molten carnauba wax is brushed on the outer side of the flexing sample. It is necessary to cover only the portion of the strip around the hub. As soon as separation begins, the temperature of this section increases very rapidly and the wax melts. The melting of the wax starts with a small area and gradually spreads as separation increases. This serves as a warning that complete separation will occur shortly thereafter and eliminates the necessity of examining the sample at frequent intervals during the early part of the run. The interval between the melting of the wax (the time at which separation actually starts) and complete separation across the sample is not always constant. For example, a sample with a short flexing time will show complete separation soon after the wax melts, whereas a sample with a greater flexing time might require two or three times as long. However, among samples having similar flexing times, the interval between the melting of the wax and com-

plete separation is fairly constant. The time of complete separation is a matter of judgment by the operator. Strips are inspected for separation by freeing one end from the jaw, bending in reverse position, and looking through.

In the case of belting which is run on a 3.175-cm. (1.25-inch) hub, the temperature obtained is not sufficient to melt the wax, and therefore the wax method is not used for belting.

No attempt is made to control temperature or humidity conditions during the flexing operation. For pads of the same construction, run at room temperature over a period of more than a year and a half, embracing approximately fifty different tests, a general agreement within  $\pm 10$  per cent has been found. Undoubtedly an arrangement controlling these conditions would be some improvement. The important point, however, is that all judgments be based on comparative tests in which the temperature effect is largely eliminated. Each group of cures, for example, will contain a pad of which the flexing properties are well known. The experimental stock is then judged by comparison with this pad, in flexing tests run at the same time.

The flexing time can be recorded in minutes or in cycles, but the latter is preferable since it largely eliminates the effects of variations in the speed of the machine.

#### Corrections

It has been pointed out that the flexing time is greatly influenced by differences in the volume of rubber in the pad. Although there is bound to be some difference in the weight of pads, this is kept as small as possible. Out of fifty pads, forty-eight weighed between 179 and 196 grams, and forty-two between 183 and 194 grams.

It is possible to determine the deviations caused by variations in the weight, and to plot a curve, from which a correction factor can be determined. This factor probably varies with different types of stocks and fabrics, but the principle is the same for all cases. The method is illustrated by the following example:

For a standard pad after it is built up, but before it is cured, we assume that a skim coat of exactly 0.051 cm. (0.020 inch) has been applied to each of the six  $12.7 \times 20.3$  cm. ( $5 \times 8$  inch) plies. By actually weighing such a pad of a certain composition (188 grams), subtracting the known weight of the fabric (76.5 grams), and dividing by the specific gravity of the compound (0.98), the volume of the rubber compound is found to be 114 cc. From this figure the ideal weight of a like pad using a compound of different specific gravity may readily be calculated.

For this standard pad it has been found by testing pads of various weights that in the region of the correct weight the flexing life varies about 2 per cent per gram deviation in weight, being longer for overweight pads and shorter for underweight pads. Therefore, if the pad weighs 193 grams the correct flexing life is 90 per cent of the observed figure; if it weighs 183 grams the correct flexing life is 110 per cent of the observed. In dealing with stocks having a different specific gravity, allowance must be made for this fact, since it is the volume, and not the weight, of rubber that counts.

## Consistency of Results

Considering the nature of the test, it yields results of a good degree of consistency. Two sets of results obtained with pads of different composition are shown in Table I. Each set consists of four strips cut from the same pad.

Table I—Flexing Results with Strips from Same Pad

PAD I		PAD II	
Melting point of wax	Observed separation	Melting point of wax	Observed separation
Kilocycles	Kilocycles	Kilocycles	Kilocycles
33.8	43.1	25.5	31.5
34.9	41.2	31.9	35.8
33.7	42.0	25.6	30.3
35.1	42.1	26.6	32.5

Table II gives results when the entire test is repeated, starting with a fresh lot of stock in each case. Dates are included to give some idea of probable temperature and humidity condition.

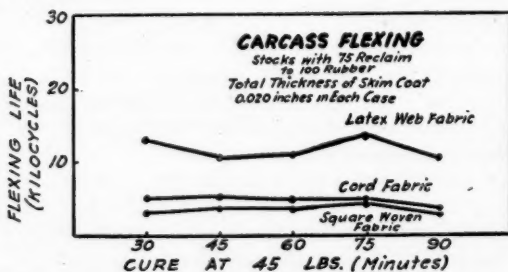


Figure 2—Flexing Life with Rubber-Reclaim Friction and Skim Coats

Table II—Reproducibility of Flexing Results in Different Runs

CURE AT 45 LBS. (3.2 KG. PER SQ. CM.)		TEST 1 1/31/29	TEST 2 3/20/29	TEST 3 3/26/29	TEST 4 6/3/29	TEST 5 6/29/29
Min.	Kilocycles	Kilocycles	Kilocycles	Kilocycles	Kilocycles	Kilocycles
30	37.6	34.1	36.4	38.7	38.4	
45	47.7	47.2	50.2	46.7	48.1	
60	53.3	83.6	51.7	56.7	59.1	
75	59.1	61.8	51.8	63.3	63.8	
90	54.9	71.3	62.5	70.7	59.7	

The correct cure on this stock is from 45 to 60 minutes. Comparing the values at these cures, it will be seen that in general the agreement is good, with the exception of the 60-minute cure on the second test.

The values obtained vary greatly with the conditions, and Table III shows the results obtained with a variety of types of stocks and fabrics. The stocks used for frictioning and skim coats are listed below. For frictioning the square woven fabric and cord fabric, it is necessary to use a larger amount of softener in formula B, 12 parts of mineral oil representing about the minimum. This will have the effect of reducing the flexing value somewhat, but to an extent insignificant in comparison with the differences shown between the cord fabric and latex web fabric. The data are shown graphically in Figures 1 and 2.

	FORMULA A	FORMULA B	FORMULA C
Smoked sheets	50	50	50
Pale crepe	50	50	50
Whole-tire reclaim	..	..	75
XX Zinc oxide	5	5	5
Light mineral oil (No. 8)	5	12	8
Sulfur	3.75	3.75	3.75
Heptene	0.5	0.5	0.5

Table III—Comparison of Different Fabrics and Compounds

FABRIC	STOCK	FLEXING LIFE FOR VARIOUS CURES <sup>a</sup>				
		30	45	60	75	90
		min. Kilo- cycles	min. Kilo- cycles	min. Kilo- cycles	min. Kilo- cycles	min. Kilo- cycles
Square woven	All rubber friction and skim coat (formula B)	5.8	8.3	10.0	11.0	9.8
Cord	All rubber friction and skim coat (formula B)	10.3	12.4	13.1	13.6	12.7
Latex web	All rubber skim coat (formula A)	38.4	48.1	59.1	63.8	59.7
Square woven	Rubber-reclaim friction and skim coat (formula C)	3.1	3.7	3.5	4.2	2.7
Cord	Rubber-reclaim friction and skim coat (formula C)	5.0	5.2	4.8	4.8	3.5
Latex web	Rubber-reclaim skim coat (formula C)	12.8	10.5	10.8	13.5	10.5

<sup>a</sup> All cures at 45 lbs. (3.2 kg. per sq. cm.).

### Meaning of Test

This test gives useful information as to the resistance of various rubber stocks, and combinations of rubber stock and fabric, to separation from flexing. The experience of this company has shown that these tests in general give a good indication of what happens in a tire. It is not possible, however, to restate the test in terms of mileage. This has been attempted with fair success for abrasion, but it must be remembered that there are some fundamental differences between the two tests. Abrasion is an effect which can be measured continuously; it is not only progressive, but its progress can be measured. We are actually measuring the effect itself when we gage a tread that has been run on the road or an abrasion slab in a laboratory test. In the case of the flexing test we are interested in the resistance of the structure to fatigue, but we cannot measure this; we can only measure the time elapsing before the occurrence of one of the effects of fatigue—namely, separation. This may be influenced by other factors as well in the case of a tire.

Nevertheless, although no attempt is made to convert kilo-cycles into miles on the road, this test has been found extremely useful as an aid to experimentation. It gives information regarding compounding ingredients, aging, the use of antioxidants, the effect of treating fabric with latex, and the effect of various calendering and curing conditions.

## Determination of Total Moisture in Carbon Blacks<sup>1</sup>

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**I**N THE course of an extended research on various grades of carbon black, determinations of total moisture were made by an adaptation of an old method. The method used was similar to one described by Allen and Jacobs (1) for measuring water in tar. The chief difference in the present method is that small amounts of moisture in carbon blacks must be weighed, whereas the larger amounts in tar could be measured. The difficulties in weighing the evolved moisture are described in the ensuing method of determination.

Five grams of carbon black were placed in a 500-cc. round-bottom flask with 25 to 35 cc. of dry xylene and 200 cc. of dry mineral oil. A short air condenser led to the bottom of a 25-cc. distilling flask, which in turn was connected to two or more calcium chloride tubes. The flask containing the sample was heated to 150–175° C. in an oil bath, a stream of dry nitrogen being passed through the apparatus. The water and xylene were distilled into the small distilling flask and thence, by warming in a water bath, into the calcium chloride tubes, the current of nitrogen being continued. It required but a few minutes to remove the water from the xylene, indicated by the disappearance of cloudiness, and the calcium chloride tubes were then connected directly to the nitrogen line and the gas was passed through until the tubes reached constant weight. Xylene is not adsorbed by calcium chloride and nitrogen does not remove water from it at room temperature during the time required for the experiment. The increase in weight of the calcium chloride tubes is the amount of water in the sample of carbon black. The amount of water thus determined is considerably higher than the 105° C. oven loss in 5 hours, and indicates that most of the moisture is of the "bound" or "capillary" type.

<sup>1</sup> Received June 13, 1929.



A comparison of the moisture as determined by the xylene method and the 105° C. oven is shown in the table:

BLACK	TOTAL 105° C.		BLACK	TOTAL 105° C.	
	H <sub>2</sub> O %	Loss %		H <sub>2</sub> O %	Loss %
Micronex No. 1	5.75	1.42	High-temperature black <sup>b</sup>	0.87	0.30
Micronex No. 2	5.96	1.85	Acetylene black No. 1	3.19	0.07
Micronex No. 3	5.20	1.56	Acetylene black No. 2	3.67	0.07
Heated Micronex (950° C.) <sup>a</sup>	0.98	0.00	Goodwin	1.50	0.33
Cabot No. 1	4.88	1.79	Thermatomic (Special)	1.25	0.10
Cabot No. 3	3.54	1.66	Lampblack	6.75	3.26
Cabot No. 2	5.41	1.57	Super-Spectra	1.07	0.10
			Zinc oxide <sup>c</sup>	0.75	0.02

<sup>a</sup> Heated 10 minutes at 950° C. in a closed crucible.

<sup>b</sup> Made at 1500° C.

<sup>c</sup> Added for comparison.

The relationship of this "bound" moisture to any physical property of a rubber mix containing the black could not be shown. It is probable that other characteristics of the black, such as adsorptive capacity, particle size, etc., are more effective in causing variations than the amount of moisture. Nevertheless the large amount of water in blacks as compared with that in other pigments, such as zinc oxide, is indicative of their relative adsorptive capacities.

- (1) Allen and Jacobs, *Orig. Com. 8th Intern. Appl. Chem.*, **10**, 17 (1912); *C. A.*, **6**, 3178 (1912).